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DEVELOPMENT OF INSTRUMENTATION FOR MEASUREMENT OF STATIONARY SOURCE ALDEHYDE, ORGANIC ACID, AND AMINE EMISSIONS

J. Daniel Bode

Bendix Research Laboratories

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16. Abstracts The goal was the development of analytical instrumentation to field monitor the major odorous compounds emitted from animal rendering plants. The program consisted of three phases; preliminary investigation, prototype development, and field testing of the instrument in a rendering plant. The recommended analytical methods suitable for field monitor development are summarized. They are grouped according to the class of compounds; aldehydes, acids, and amines. The laboratory experiments showed that the 3-methyl-2-benzothiazolone (MBTH) aldehyde method, the ninhydrin measurement for amines, and the ferric ammonium sulfate - ortho - phenanthroline method for organic sulfur compounds (oxidized to SO_2) offered the best promise of adaption for tape monitoring instruments. The analytical methods, laboratory tests, and design and development problems for each monitor are presented. Final testing of the monitors in a rendering plant led to minor modifications. Comparison of several amine and sulfur monitor readings with odor panel evaluation of concurrent samples showed these instruments could record concentrations at or below the Federal guideline concentration of 5.6 OU/cu. meter. More extensive and systematic field tests are clearly indicated as the next step in developing this type of instrument for automatic, low cost odor monitoring.

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Field monitor

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PHASE I

PRELIMINARY INVESTIGATIONS

SECTION 1

INTRODUCTION AND SUMMARY

The ultimate goal of this development program was analytical instrumentation to field-monitor the major odorous compounds emitted from animal rendering plants. The program consisted of three phases: Phase I - Preliminary Investigation to determine practical methods for measuring the individual odorous compounds and for monitoring the principal classes of odorous compounds, Phase II - Prototype Development to produce field usable instruments for class compound monitoring, and Phase III - Field Testing of the Instruments in a rendering plant. Earlier studies had identified aldehydes, carboxylic acids, and amines as among the most odorous compounds emitted in the cooking, rendering, and decay of meat and offal. The program plan, therefore, called for developing monitoring instruments for these three classes of organic compounds or for a representative member of each class.

The work in Phase I was carried out with two objectives: first, an analysis technique to determine the major odorous compounds in rendering plant emissions and, second, selection of chemical analysis techniques suitable for development for field monitors for aldehydes, organic acids, and amines. The wide variety and low concentration of compounds present in rendering plant emissions made gas chromatographic separation the most practical way to analyze for the odorous constituents. Analysis was based on cross-correlating retention times on different chromatographic columns using a sniffing port to detect the odorous components. Table 1 lists all of the odorous compounds found in this study as well as those reported in two other studies. The presence of a large number of organic thiols and sulfides and their more obnoxious odors compared to the organic acids present led to the replacement of the organic acid monitor by an organic sulfur monitor.

The obnoxiously odorous compounds actually represent only a small fraction of the vapor emissions from rendering plant operations. Of these, the thiols and sulfides have the most intense and objectionable odors even at extremely low concentrations. The normal aldehydes, acids, and amines rank next, requiring higher concentrations, in that order, to cause an objectionable odor. The aldehydes found highest in concentration were 2-methylbutanal, 3-methylbutanal, and 2-methylpropanal, which probably have the least objectionable odor of the low molecular weight aldehydes. Ethanal (acetaldehyde), methanal (formaldehyde), propanal, and hexanal ranked intermediate in concentration but much higher in objectionable odor. The other aldehydes, the acids, and the amines ranked more than an order of magnitude lower in concentration along with the thiols and sulfides. Non-odorous hydrocarbons (alkanes), faintly odorous ethanol and methanol, and propanone (acetone), 2-butanone, and 2-hexanone made up the largest part, 50-70%, excluding water vapor, of many of the samples.

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Table 1 - Compounds Found in Rendering Emissions

Compound Class	Compound	Found By - X		
		BRL[+]	IITRI[++]	ELW[+++]
Aldehydes	Methanal (Formaldehyde)	-	-	X
	Ethanal (Acetaldehyde)	X	X	X
	Propanal	X	X	X
	n-Butanal	X	X	-
	n-Pentanal	X	X	-
	n-Hexanal	X	X	X
	n-Heptanal	X	X	-
	n-Octanal	X	X	-
	n-Nonanal	X	X	-
	2-Methylpropanal	X	X	X
	2-Methylbutanal	X	X	-
	3-Methylbutanal	X	-	X
Acids	Methanoic (Formic)	(X)	-	X
	Ethanoic (Acetic)	(X)	X	X
	Propanoic	X	X	X
	Butanoic	(X)	X	-
	Hexanoic	(X)	-	-
	2-Methylpropanoic	(X)	-	X
	3-Methylbutanoic	-	X	-
Amines	Methylamine	(X)	NR*	X
	Dimethylamine	(X)	NR*	-
	Ethylamine	(X)	NR*	-
	Propylamine	X	NR*	-
	Butylamine	X	NR*	-
	Hexylamine	X	NR*	-
Thiols	Methanethiol	X	-	X
	Ethanethiol	X	-	X
	Propanethiol	X	-	-
	Butanethiol	X	-	-
	Pentanethiol	X	-	-
	Nonanethiol	X	-	-
	1-Propene-3-thiol (Allylmercaptan)	X	-	-
Sulfides	Hydrogen Sulfide	X	-	X
	Dimethyl Sulfide	(X)	-	X
	Diethyl Sulfide	X	-	-
Alcohols	Methanol	X	-	X
	Ethanol	X	X	X
	Propanol	X	X	-
	Butanol	X	X	-
	Pentanol	X	X	-
	Hexanol	X	-	-
	Isopropanol	X	X	-
	1-Penten-3-ol	X	X	-
Ketones	Propanone (Acetone)	X	X	X
	2-Butanone	X	X	X
	3-Pentanone	X	-	-
	2,3-Butanedione	X	X	-
Alkenes	1-Octene	X	-	-
	1-Decene	X	-	-
Aromatics	Benzene	X	X	X
	Toluene	X	X	-
	p-Dichlorobenzene	X	X	-
Others	Acrylonitrile	(X)	X	-
	2-Methyltetrahydrofuran	X	X	-

47 7823

[+] Bendix Research Laboratories

[++] Illinois Institute of Technology Research Institute[4]

[+++] E. L. Wick[14]

* Not Reported

(X) Found on only one type of chromatographic column

The objectionable odor of rendering plant emissions, it must be concluded, arise from a mixture of many highly odorous compounds (thiols, sulfides, aldehydes, acids, amines, and some higher alcohols) present in very low concentrations. Class analysis, therefore, is the best approach to monitoring the odorous emissions.

SECTION 2

SAMPLING AND ANALYSIS

2.1 COLLECTION TECHNIQUES

Samples were collected at four different sites in a local rendering plant over a period of four months. Three of the sites, two different press vents and the exhaust line from the condenser, provided high enough concentrations of the emission compounds to make separation and identification practical without recourse to mass spectrometry or tedious microchemistry. The fourth site, the exhaust fan room, gave concentrations typical of the ambient air inside the plant.

Most of the samples were collected in cold-traps consisting of two or three glass tube fingers (straight or Allihn bubble type) connected in series and cooled with either dry ice or liquid nitrogen. Freezing of water in the traps posed the major and essentially unsolvable problem with low temperature cold-trap collection. Both 3A-Molecular Sieve and calcium sulfate drying filters proved impractical for removing the water. The molecular sieve had too low a capacity for a practical size filter, and the calcium sulfate adsorbed the organic compounds.

Five different cold trap arrangements, listed in Table 2, gave different collection efficiencies and collection times before freezing shut. The initial sampling rate was always 5 ℓ/min (10 cfh) but decreased with ice formation in the traps. Complete plugging usually occurred within two hours even starting with the cold fingers only about one-third immersed in the coolants. The longest collection time, 2-3/4 hr, was achieved with the triple-U arrangement starting with the cold fingers about one-third immersed. All three traps filled completely with ice and sample in this time without fully plugging.

Figure 1 shows the triple series traps on the metal frame used to hold them near the sampling source at the rendering plant. Tubing connections between the traps were Teflon and the sampling line was 3 mm ID Teflon tubing with 1.5-mm wall thickness wrapped with electrical heating tape. A 28-cm long section of stainless steel tubing (4 mm ID, 1-mm wall) served as a probe at the end of the sample line to take samples from the press vents. The condenser exhaust line had a petcock sample port suitable for direct connection to the sampling line. A separate rack held the sampling pump with particle pre-filters and flow meters, power outlets and controls for the electrical heating tapes, and a thermocouple meter and selector switch to measure sampling line temperatures. Figure 2 shows the complete sampling unit. The inlet to the sample pump was fitted with an "X" connection so the pump could pull sample gas through two different collectors at the same time with a gage to monitor the partial vacuum.

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Table 2 - Cold-Trap Collection Trains

Series	Trap #	Coolant	Type of Cold-Finger Tube
Double	1	Dry ice/2-methoxyethanol*	Straight
	2	Liquid N_2	Straight
Triple-A	1	Dry ice/2-methoxyethanol*	Straight
	2	Liquid N_2	Allihn bubble
	3	Liquid N_2	Allihn bubble
Triple-B	1	Liquid N_2	Straight
	2	Liquid N_2	Centrifugal inlet
	3	Liquid N_2	Allihn bubble
Triple-C	1	Ice/water	Straight
	2	Liquid N_2	Centrifugal inlet
	3	Liquid N_2	Straight
Triple-D	1	Dry ice/2-methoxyethanol*	Straight
	2	Liquid N_2	Centrifugal inlet
	3	Liquid N_2	Straight

67 8023

*Methyl Cellosolve

Samples were also collected on activated charcoal, on 13X Molecular Sieve, and in 1% sodium bisulfite aqueous solution. The charcoal and Molecular Sieve were packed in stainless steel tubes, 1.2 cm ID and 30 or 50 cm long, with sample gas flows of 3 ℓ/min with the shorter tubes and 4 ℓ/min with the longer tubes. Activated charcoal at ambient temperature collects the least amount of water and offers the only practical way to make sample collections over a long period of time from moisture-saturated atmosphere. However, if the sample cannot be eluted and analyzed immediately after collection, the packed tubes should be refrigerated at -10°C or colder to retard chemical interactions on the charcoal surface. The Molecular Sieve saturates with water and gives much of it up when the sample is eluted. Figure 3 shows the activated charcoal collector with three parallel collection tubes that was used to sample the ambient exhaust fan room air at the rendering plant. Samples were collected for 13.5 hr at 3 ℓ/min flow during the overnight working hours at the plant. The bisulfite solution collects and preserves aldehydes by converting them to the bisulfite addition compounds. These solutions were checked for formaldehyde and pyruvic aldehyde using chromotropic acid.

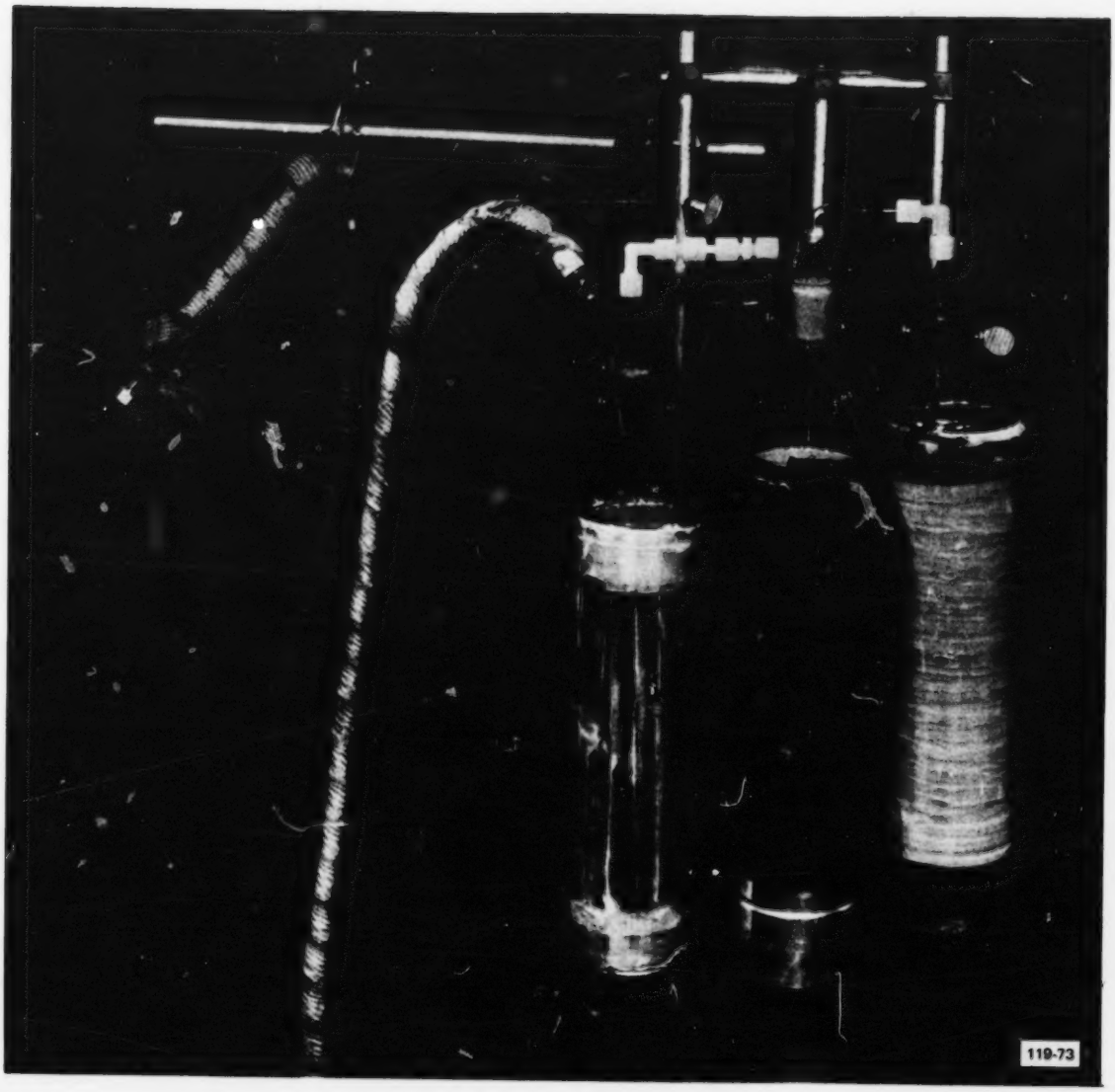


Figure 1 - Cold Trap Collection Tubes

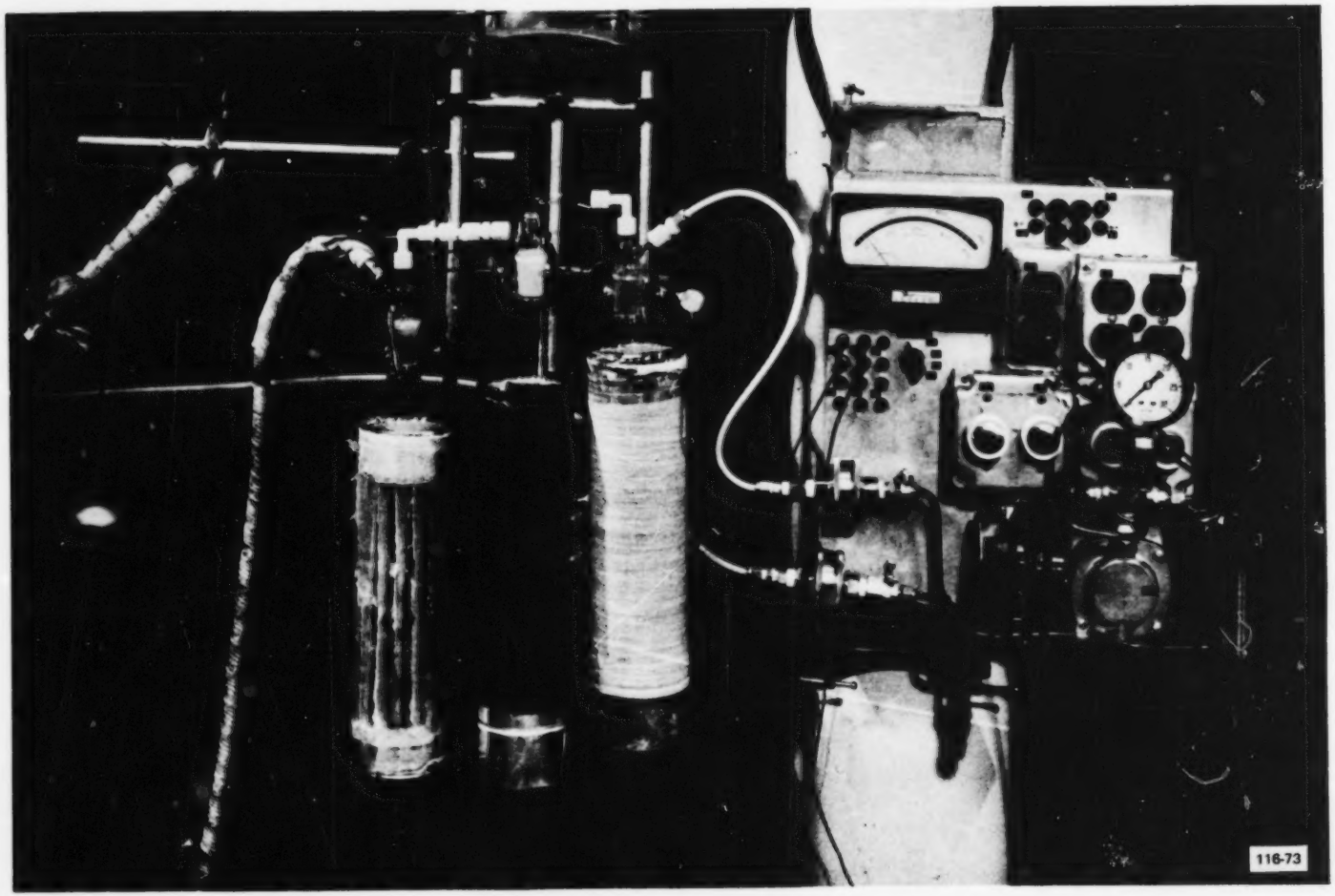


Figure 2 - Complete Collection Train

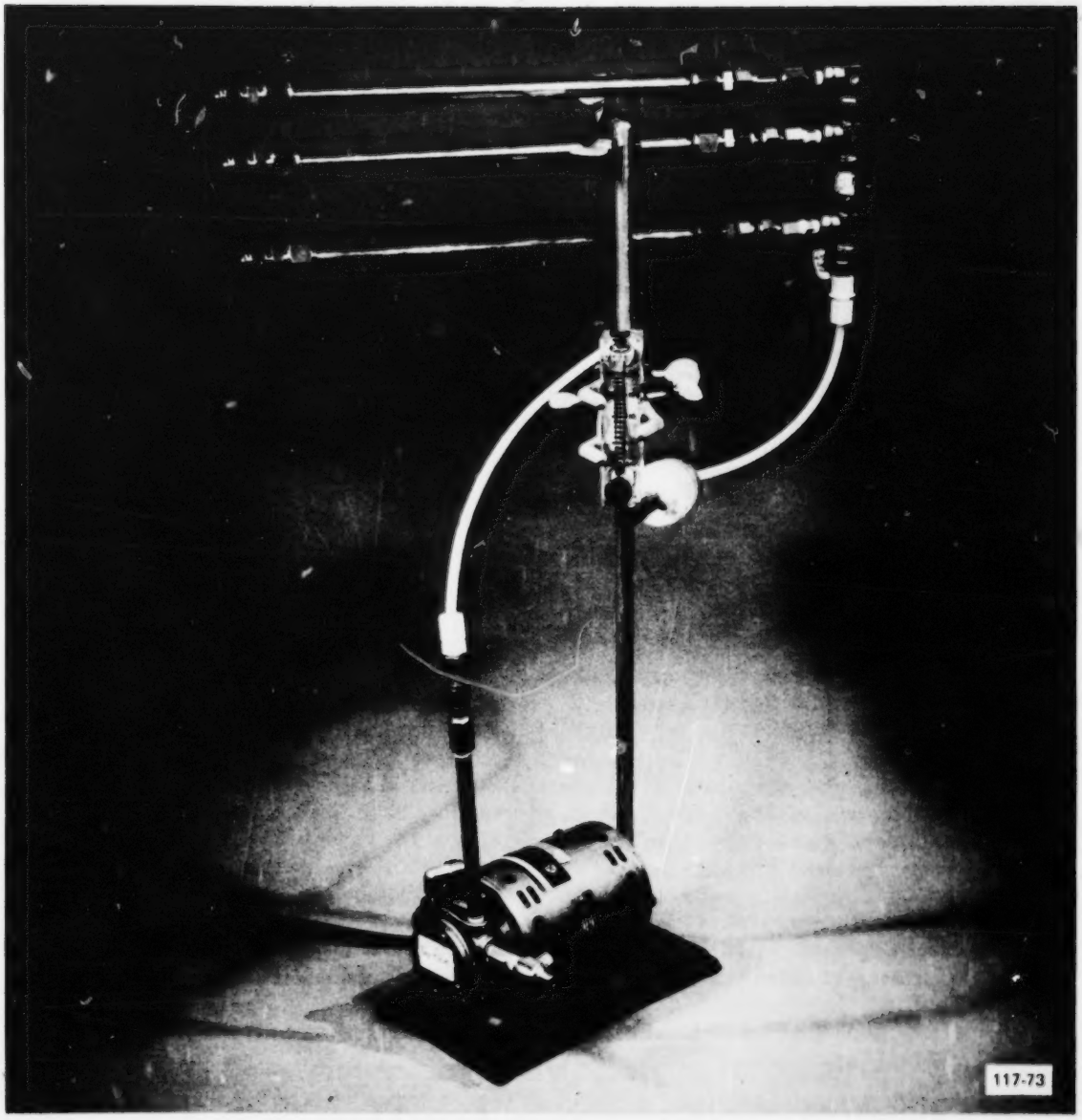


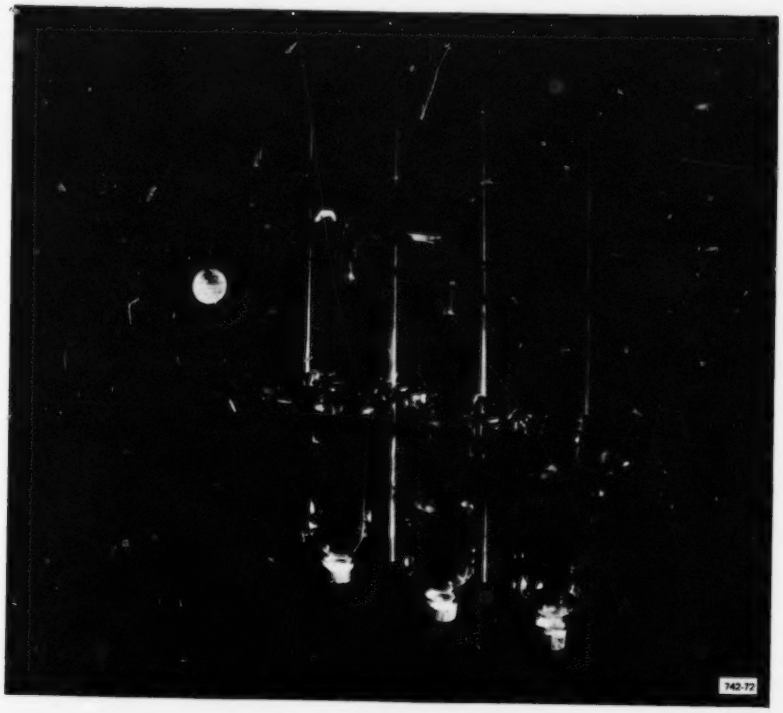
Figure 3 - Activated Charcoal Collector

2.2 ANALYSIS TECHNIQUES

Separation and correlation of retention times on different chromatographic columns served as the principal analytical method for identifying the odorous compounds in the collected samples. All the samples collected in cold traps were kept at liquid nitrogen temperature (-196°C) until analyzed. Samples collected on activated charcoal and the Molecularlar Sieve were stored in the freezing compartment of a refrigerator until analyzed. The large amount of water present in the samples made the concentration of odorous compounds too small for reliable, direct analysis. Thermal partitioning of the samples before chromatographic separation eliminated most of the water. The partitioning apparatus, shown in Figure 4, consisted of three glass cold traps made with 14/35 standard taper glass joints with the dimensions shown in Figure 5. The first trap, cooled in an ice/salt water bath had a 12 cm long cold finger to collect the water transferred during partitioning. The others had 7.5 cm long cold fingers. The second trap was cooled in a dry ice/2-methoxyethanol (Methyl Cellosolve) bath and the third in liquid nitrogen or liquid argon. The partitioning consisted of passing pure nitrogen gas at 0.05 ℓ/min through the sample trap, initially at liquid nitrogen temperature, then through the three series cold traps. The sample trap, suspended from a ring stand in the ambient air, gradually warmed to room temperature with the nitrogen flowing. Finally, immersing the trap in successive beakers of hot water (90-95°C) forced out the less volatile compounds with a minimum amount of water vapor being transferred into the first partition trap. The partitioning was continued for two to three hours depending on the sample size.

After partitioning was complete, the traps were separated, immediately stoppered by forcing lightly greased (Apiezon 101) serum bottle stoppers (6 mm top diameter) into the hemispherical joint openings, then stored in dry ice pellets or chips. Most of the rendering plant samples contained only enough organic material to give a thin liquid-film condensate on the partition trap walls. This was transferred to the gas chromatograph by inserting a 5 cm (2 in.) long syringe needle on a 30 ml syringe through the septum portion of the serum stopper, then drawing out the vapor sample as the partition trap was warmed over a hot plate or in hot water. Vapor samples were injected immediately into the gas chromatograph. For the few samples that gave enough liquid condensate in the partition trap for direct liquid sampling, the traps were separated at the standard taper joint and sealed with a large size (16 mm top diameter) serum bottle stopper. Samples were then transferred with a 10 μℓ syringe.

Separations were made on four different gas chromatographic columns under the conditions listed in Table 3. The injection port and the outlet lines were kept around 250°C. The effluent from the column was split with half going to a flame ionization detector (FID) and the other half out through a sniffing port. The stainless steel tubing leading to the sniffing port was heated to around 200°C and carried the gases up through



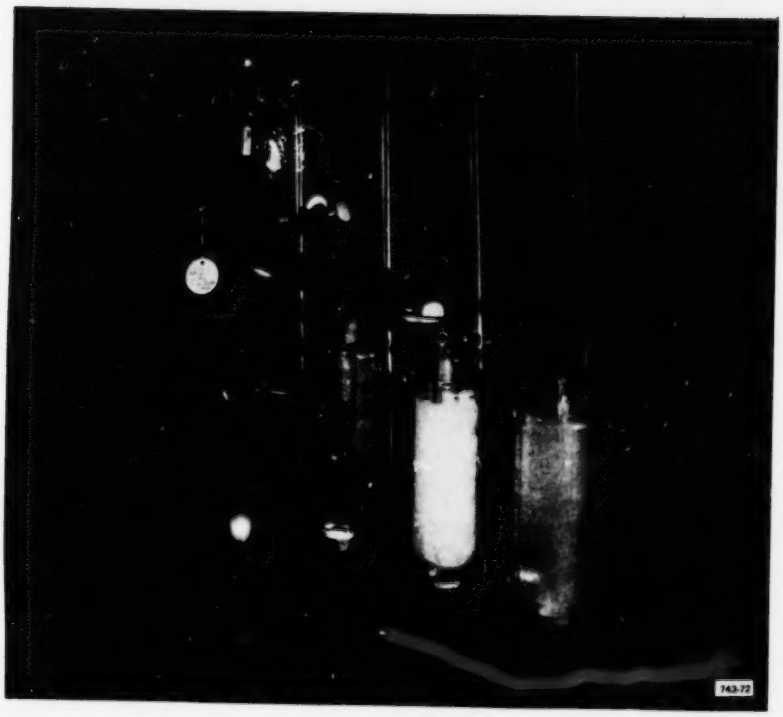


Figure 4 - Thermal Partitioning Apparatus

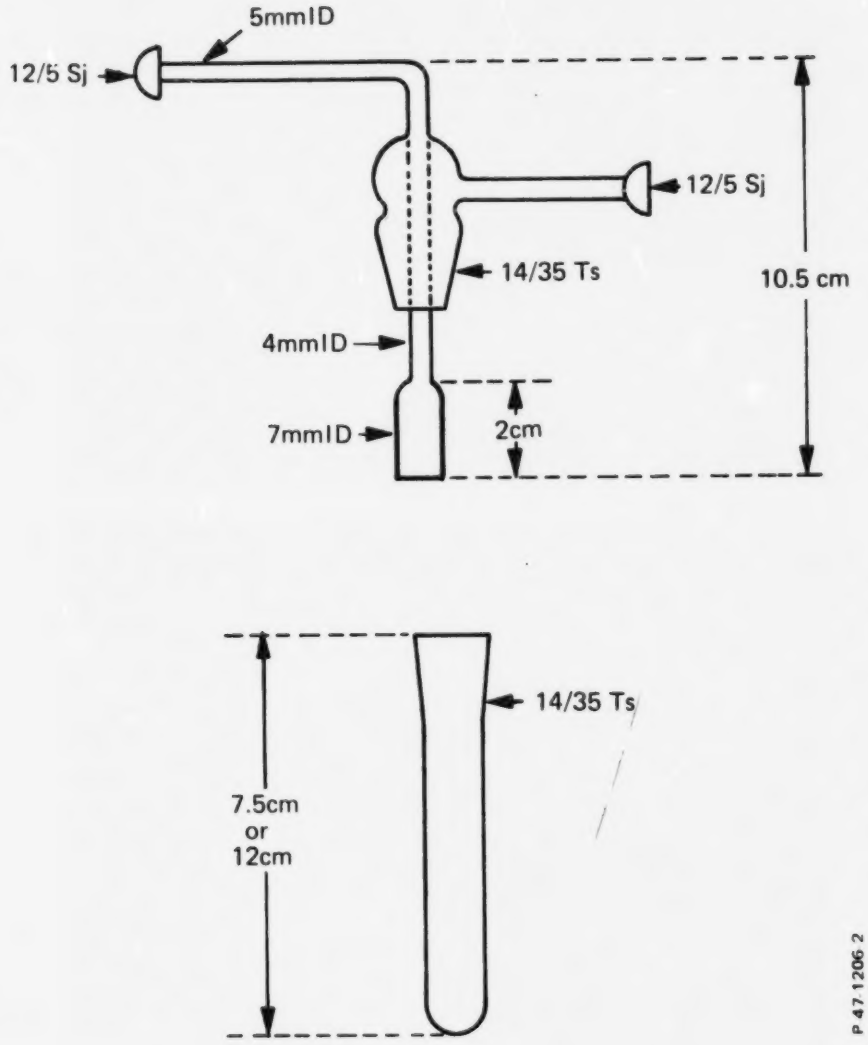


Figure 5 - Partition Cold Trap

Table 3 - Gas Chromatographic Columns

Column Number	Column Length, m*	Stationary Phase	Support	Temperature Program, °C	Heating Rate, °C/min	Carrier Gas	Carrier Flow, ml/min
5	5	Carbowax 20M (20%)	Chromosorb P-AW (80-100 mesh)	60-250	4	He	25
9	6.6	Apiezon-L (10%)	Chromosorb P-AW (80-100 mesh) DMCS	60-250	3	He	34
12	3	DEGA + H_3PO_4 (25% + 2%)	Chromosorb W-AW (80-100 mesh) DMCS	100-220	4	He	25
13	3	Pennwalt 223 (28%)	Gas Chrom R (80-100 mesh)	75-180	3	He	34

47.762-3

*Column tubing - stainless steel (316), 2mm ID, 3mm (1/8 in.) OD.

the center of a Teflon cylinder 5 cm in diameter and 5 cm high. An annular space between the stainless steel tube and the surrounding Teflon cylinder let cool, humidified air mix with the hot effluent gases in a shallow cup-shaped depression in the top of the cylinder. Figure 6 shows the sniffing port on the Bendix 2500 Gas Chromatograph used for all the chromatographic separations. Odor notations were made directly on the chromatogram as the fractions eluted.

Samples collected on activated charcoal and Molecular Sieve were partitioned by eluting the vapors into the thermal partitioner. Pure nitrogen gas was passed through the collector tube at 0.05 ℓ/min and into the partition traps while the collector tube was slowly heated in a tubular furnace to 350°C. After partitioning, these samples were stored and chromatographed as described above for the samples collected in cold traps.

The difference in molecular properties of the different classes of compounds found in rendering emissions makes complete separation of all the compounds on one gas chromatographic column impossible. This means many of the chromatographic fractions from a given column will contain two or possibly more compounds. Collection and subsequent separation of individual fractions on a different column is not practical for the analysis of many samples because the volume of each fraction is so small and the technique too time consuming. Figure 7, for example, shows the chromatogram from an Apiezon-L column separation of 13 ml of sample vapor from the third, liquid argon cooled, trap of the thermal partitioner. In this sample, two fractions make up over 50% of the volume while the remaining 5-6 ml are distributed among 43 other fractions.

Different samples analyzed on different columns, however, provide a simple, more rapid method of identifying fractions by cross-correlating retention times for specific compounds. If the different columns vary sufficiently in stationary phase polarity, the retention times for different classes of compounds will vary greatly between them. Zarazir, Chovin, and Guiochon[15] recommend three different columns; SE30 (a non-polar silicone), Carbowax 20M (polyethyleneglycol), and PGS (polyethylene glycol succinate). Four different columns were used in this study; Apiezon-L (non-polar hydrocarbon); Carbowax 20M; DEGA + H_3PO_4 (diethyleneglycol adipate polymer); and Pennwalt 223 + NaOH (a Pennwalt Corp. material). Apiezon-L and DEGA + H_3PO_4 would not resolve the amines (excluding them from these chromatograms), and the Apiezon-L and Pennwalt 223 + NaOH would not resolve the organic acids (excluding them from their chromatograms). Acids and amines, therefore, could be cross-correlated on only two columns. Additional correlations would have required using more than four different columns or forming derivatives of these compounds in the samples. Time limitations on the program, however, would not permit this extra development work.

The columns were characterized with homologous series of n-alkanes, n-alkenes, n-aldehydes, branched aldehydes, n-acids, n-amines, n-alcohols, n-thiols, n-sulfides, and 2-ketones.

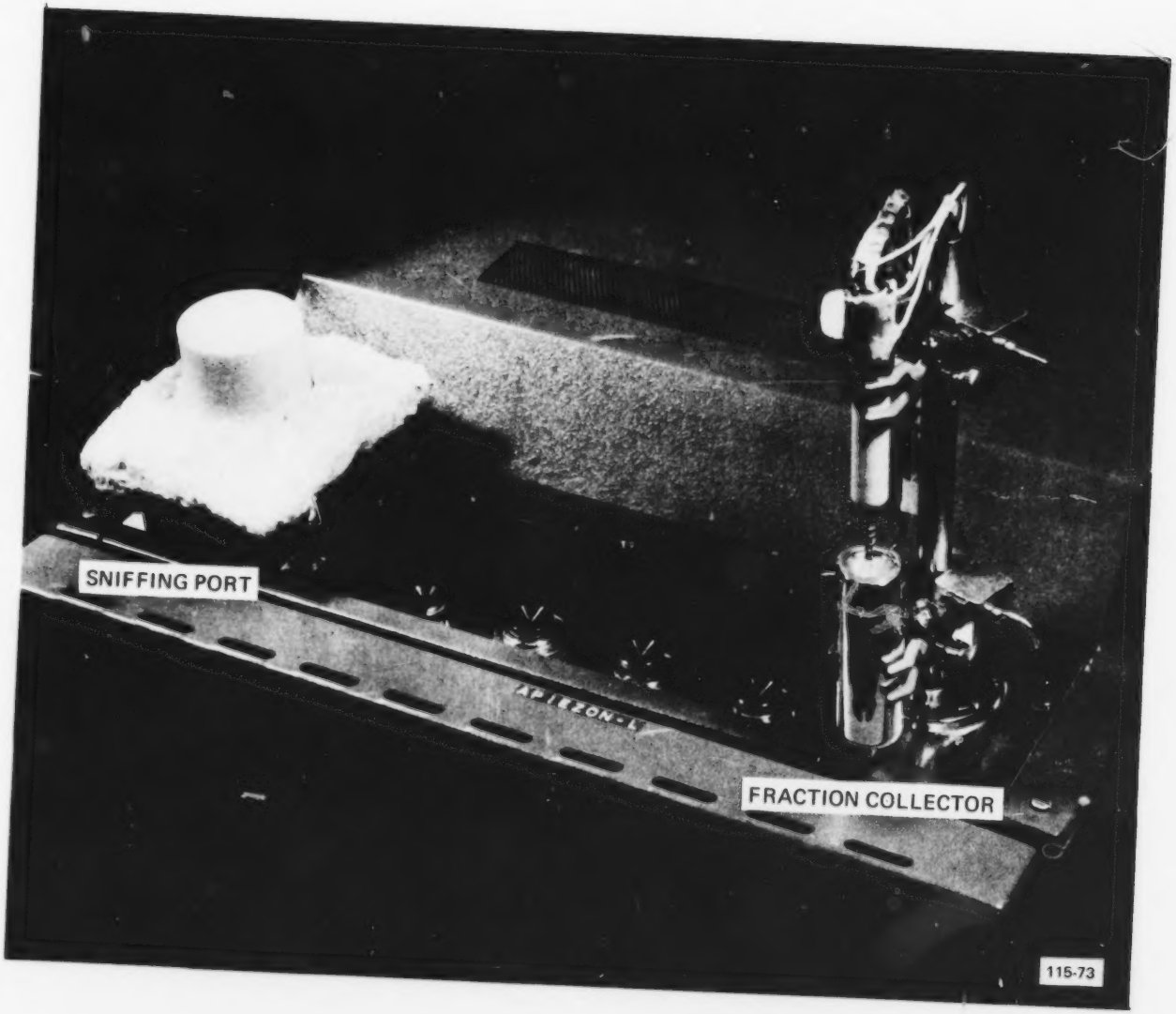
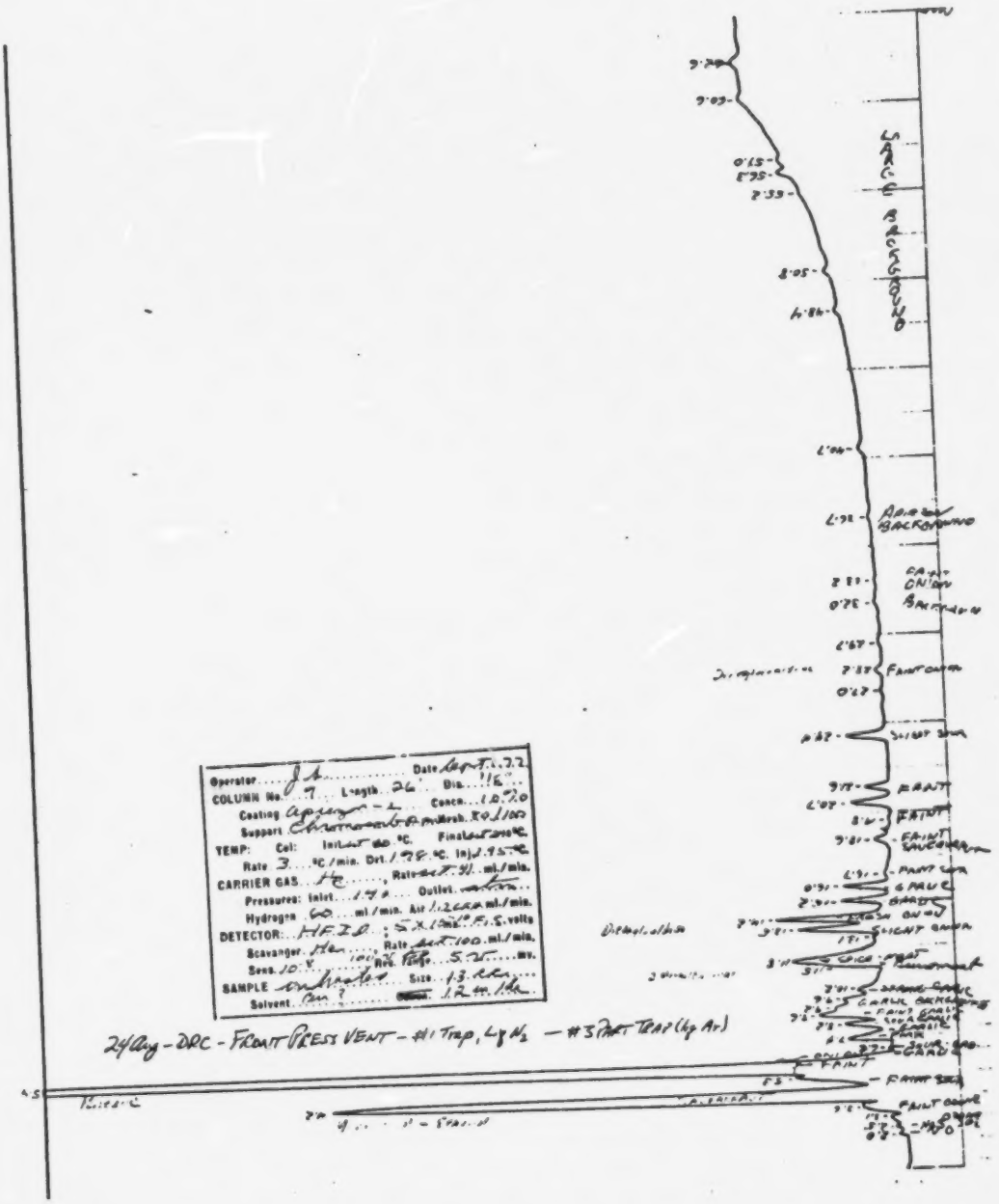


Figure 6 - Sniffing Port on Gas Chromatograph


Operator JA Date Sept. 22
COLUMN No. 7 Length 26' Dia. 1/8"
Coating Apiezon - L Conc. 10.20
Support Chromosorb W AW millrab. 80/100
TEMP: Col: Initial 60 °C. Final 200 °C.
Rate 3 °C/min. Det. 195 °C. Inj. 195 °C
CARRIER GAS He, Rate 27.3 ml/min.
Pressures: Inlet 17.8 Outlet atm.
Hydrogen 60 ml/min. Air 1,200 ml/min.
DETECTOR: HFID ; 5 X 10 F.S. volts
Scavenger He, Rate Aux 100 ml/min.
Sens. 10 V Rec. Temp. 5.25 mv.
SAMPLE Enriched Size 13 RRy
Solvent Benz 1.24 ml
24 Aug - DRC - FRONT PRESS VENT - #1 Trap, Lq N2 — #3 PMT TRAP (lq Ar)
LARGE BACKGROUND
PAINT
PAINT
PAINT

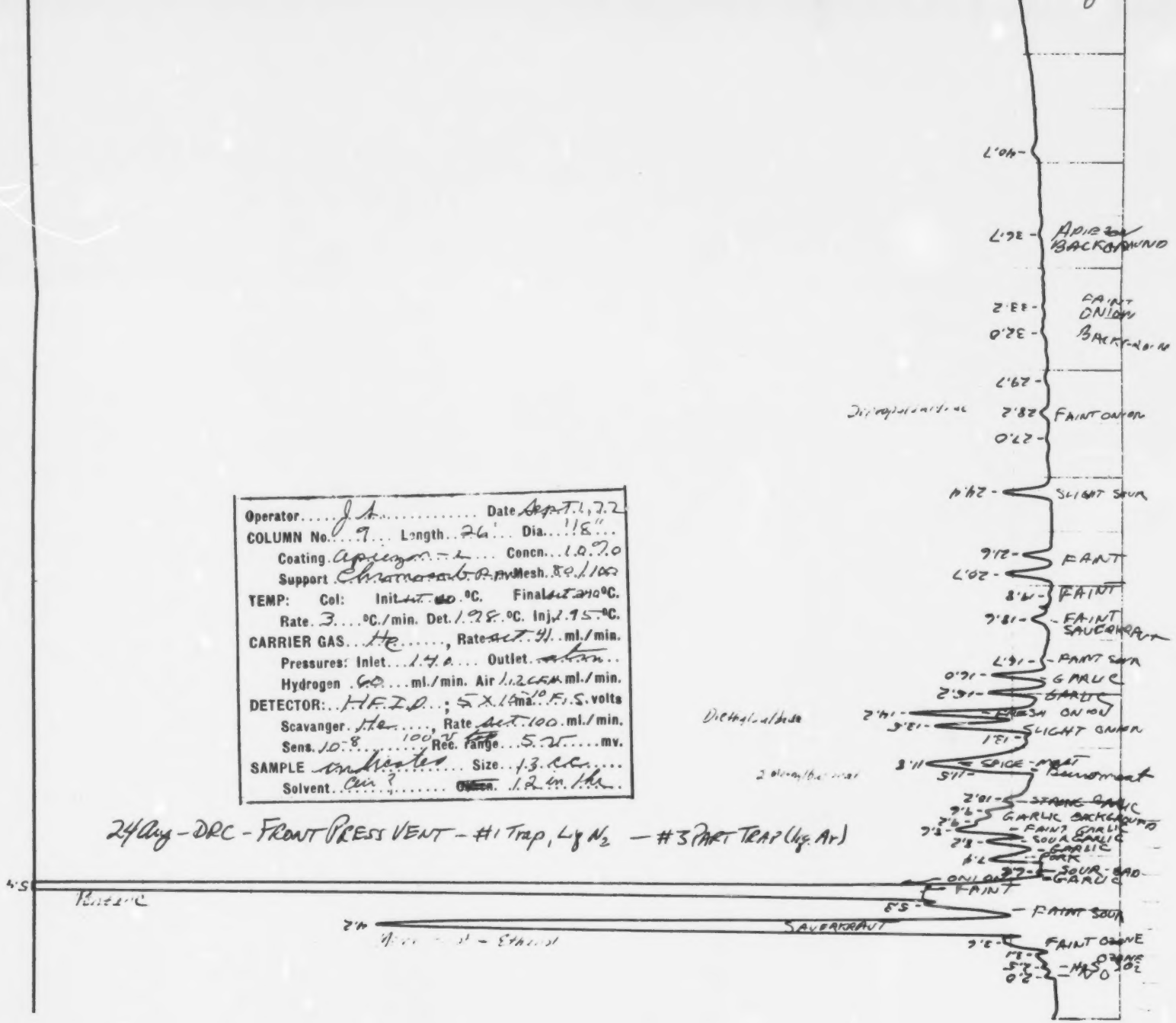
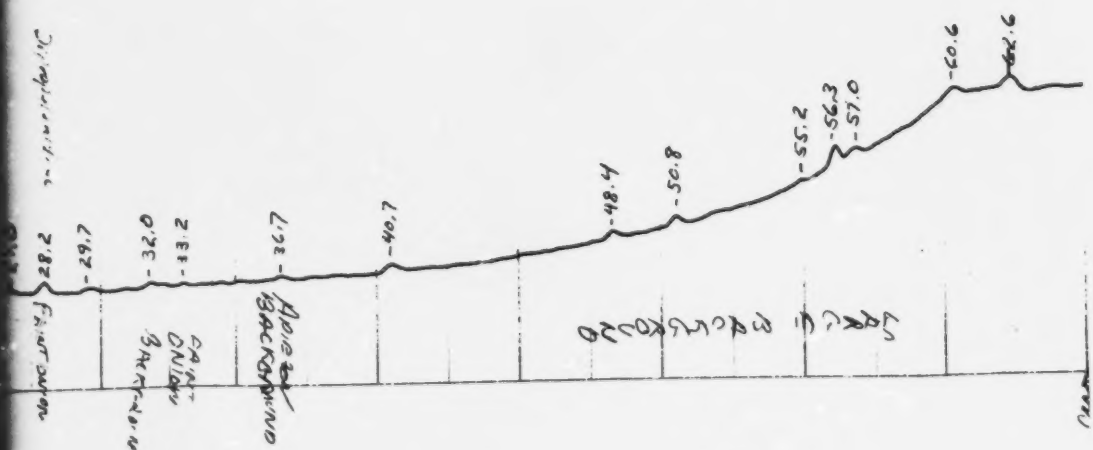


Figure 7 - Press-Vent Sample, Apiezon-L Chromatogram



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B-Vent Sample, Apiezon-L Chromatogram

Retention times were also measured for several iso-acids, iso-alcohols, dienes, allylsulfides and thiols, disulfides, aromatics, and specific compounds such as 2-methyltetrahydrofuran, t-2-hexenal, acrylonitrile, 1-penten-3-ol, etc. Standard deviations for repeated retention time measurements made during the course of the program are listed in Table 4 for the principal compound classes. The greater deviations for both acids and amines reflect the difficulty of separating these compounds directly on a gas chromatographic column unless it is specifically prepared for them to the detriment of other separations.

Table 4 - Retention Time Deviation

Compound Class	Average Standard Deviation, min
Acids	1.2
Alcohols	0.8
Aldehydes	0.5
Amines	2.8
Thiols	0.6

Because of the large number of samples analyzed, the complexity of the chromatograms, and the wide variation in concentration among different samples, direct comparison of chromatograms from a given column was not practical. To facilitate cross-correlation, therefore, retention times of odorous fractions were plotted on a vertical time scale on large graph paper with different sample separations placed side by side along the horizontal axis. Matching retention times for all the samples separated on a given column were then noted and possible compounds corresponding to these retention times were listed. Comparison of these lists of compounds for all the samples analyzed on the four different columns along with the odor notations on individual chromatograms showed which compounds were common to two or more of the columns and which fractions from a given column contained several compounds. Table 1 lists the compounds found by this cross-correlation of 72 gas chromatographic separations. With the exception of the acids and amines, which could only be separated on two different pairs of columns, all the compounds listed were found common to either three or all four of the different column separations.

Odor notations for the chromatographic fractions confirmed many of the correlations between different columns but could not furnish positive identification because of overlapping fractions and persistence of thiol and sulfide compound odors. Interference from these intensely odorous sulfur compounds was not anticipated. The report from IITRI[4] made no mention of specific sulfur compounds, giving only a total sulfur by flame emission analysis; E. L. Wick[14] reported only hydrogen sulfide,

methanethiol, and ethanethiol, all highly volatile compounds. Both odor and retention time correlations confirmed the presence of methanethiol through pentanethiol as well as allylmercaptan, allyl methyl sulfide, and diethyl sulfide in the samples analyzed for this program. Although they were not considered part of this program as initially planned, the extremely intense and disagreeable odor of these compounds forced consideration of their measurement in any attempt to monitor rendering plant emissions.

Concentrations of the odorous compounds varied widely from sample to sample, even from the same sampling site in the rendering plant. However, they fit roughly into three concentration groups. A few compounds in different combinations made up 50-70%, exclusive of water, of many of the samples. The compounds most often found in these predominant groups were:

2-methylbutanal

3-methylbutanal

2-methylpropanal

pentane

propanone

ethanal

ethanol

2-butanone

in that general order. A few other compounds were predominant in one or two chromatographic separations. These included the aldehydes n-propanal, butanal, pentanal, and hexanal; the normal alcohols methanol, propanol, and butanol; 2-hexanone; and 1-pentene.

A larger number of compounds fell into an intermediate concentration range, making up from 10-50% of the sample - again exclusive of water. Compounds in this group included

n-aldehydes: methanal through nonanal

amines: dimethyl and trimethyl

acids: 2-methylpropionic (isobutyric)

thiols: methane-, ethane-, allyl-

n-alcohols: methanol through hexanol

sulfides: hydrogen sulfide and diethyl sulfide

ketones: 2-pentanone

aromatics: toluene

alkenes: 1-octene

The remainder of the sample was made up of a large number of compounds present in very small concentrations, many of which were not identified. Based on the samples analyzed, therefore, the characteristic odor from rendering operations is not constant and results primarily from the interaction of a large number of different compounds present in moderate or low concentrations.

SECTION 3

ANALYTICAL METHODS FOR FIELD MONITORING

3.1 REQUIREMENTS

Analytical methods suitable for field monitoring instruments must be adaptable to simple mechanical operations and must have as well the requisite sensitivity, accuracy, specificity, and chemical stability. For this reason, sophisticated instrumental methods and complex chemical procedures were not considered. In particular, methods were sought that involve direct colorimetric, spectrophotometric, reflectometric, fluorometric, or electroconductimetric principles that could be used in a simple tape-monitoring type instrument. Fortunately, the most sensitive chemical analytical methods with measurable concentration limits in the parts-per-billion (ppb) or parts-per-million (ppm) range are fluorometric or colorimetric. The only major disadvantages to these types of methods for automatic field monitoring applications are the complex manual manipulations (filtrations, extractions, etc.) required for many of the procedures, the instability or incompatibility of some of the reagents under field conditions or on paper tapes, and interferences from related compounds.

The methods screened included the standard procedures as published in ASTM,[1] AOAC,[2] Welcher,[13] Siggia,[10] and similar volumes; photometric methods covered in Snell,[11] Sawicki,[9] and related books; methods specific for gaseous and air pollutants reported in books such as Stern,[12] Ruch,[7] Leithe,[6] and the recent Intersociety Committee[5] volume; as well as methods reported in cumulative and recent yearly indexes of Chemical Abstracts. The initial screening led to more than 60 possible methods for aldehydes, only 14 for organic acids, and 15 for amines. Review of original papers and simple laboratory tests reduced this list to the five aldehyde methods and three acid and three amine methods discussed in the following section.

3.2 SELECTED ANALYTICAL METHODS

The five methods selected as best suited for development for a field monitor instrument for aldehydes are

(1) Reduction of silver ion to silver metal (Tollen's method)

(2) Reduction of Nessler's reagent to mercury

(3) MBTH colorimetric

(4) Bisulfite-hydrazine colorimetric

(5) Aminobenzaldehyde and methylamine hydrochloride colorimetric

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The first two have the advantage of a simple direct reaction on an impregnated paper tape which essentially parallels the widely used lead acetate tape procedure for hydrogen sulfide. The transmittance or reflectance of the metal deposit on the tape could be measured with the photometric equipment on conventional tape sampler-monitors. Laboratory experiments using tapes impregnated with ammoniacal silver nitrate treated with aqueous acetaldehyde and acetaldehyde bisulfite solutions showed that the reactions proceeded on the tape in a few minutes time with gentle heating. The less-than-ppm sensitivity claimed for the Tollen's reagent was not achieved in this test; however, optimum conditions were not established in these tests and more sensitive modifications of the reagent were not tried. The major drawback for these metal ion reduction methods is the interference by other reducing agents, including any present in the paper tape itself. Sulfur compounds could possibly be removed with neutral or slightly acid silver nitrate or mercuric acetate which will not oxidize aldehydes. The ease of adapting these methods to tape sampler monitoring made them worth investigating despite their drawbacks.

The MBTH (3-methyl-2-benzothiazolone hydrazone hydrochloride) method has the advantages of extreme sensitivity, good specificity (especially for the water soluble, lower molecular weight aldehydes), simplicity, and widespread application for aldehyde determinations. Aldehydes react with MBTH so the reagent can collect the sample directly with only the need for subsequent addition of an oxidizing agent (ferric chloride in sulfamic acid solution) to develop the color. The major drawback to this method is the slowness of the reaction between the MBTH and aldehydes. After sample collection, the MBTH-aldehyde mixture is aged one hour to assure complete reaction. This is not a serious disadvantage for long time sampling but could interfere if short time (less than one hour) sampling is desired. Otherwise this is the preferred colorimetric method.

The bisulfite-hydrazine method also has the advantages of high sensitivity and good selectivity (again for water soluble aldehydes) and permits direct collection of the aldehydes by sodium bisulfite. 2,4-Dinitrophenyl-hydrazine, the most widely used phenylhydrazine for aldehyde determination, is reportedly stable indefinitely in phospheric acid - ethanol solution. For maximum sensitivity, however, the procedure is more complex than that with MBTH, requiring reagent addition after collection, heating for 30 min, then reaction with alcoholic KOH to develop the color. Its proved reliability in aldehyde determinations, however, made it a good back-up choice for the MBTH method.

A third possible colorimetric method which has the advantage of being specific for aliphatic aldehydes is the reaction with o-aminobenzaldehyde and methylamine. The amine condenses onto the aldehyde group of the o-aminobenzaldehyde and the collected aldehyde onto the amine group. Aliphatic aldehydes can then close a second ring forming a

1-hydro-quinazolium compound. When methylamine hydrochloride is used (because of its stability), the reagents must be added sequentially to the collected aldehyde. First the methylamine must be freed from its hydrochloride by adding sodium pyrophosphate; then the o-aminobenzaldehyde is added. The color develops in about 10 min at 25°C. The specificity to aliphatic aldehydes and more rapid reaction rate at room temperature give this method an advantage over the MBTH and bisulfitehydrazine methods. Poorer reagent stability, more mechanical steps, and poorer sensitivity, however, make it a third choice.

Fluorometric methods were considered for aldehydes but unfortunately they required either heating in concentrated sulfuric acid or manipulations too complicated to adapt for a simple field monitor.

Of the few available methods for the quantitative measurement of organic acids, only three colorimetric ones offered much hope for adaptation to an automatic field monitor. These were

(1) pH color or fluorescent indicator

(2) Phosphomolybdic acid colorimetric

(3) Ferric-5-nitrosalicylate decoloriation

The pH color or fluorescent indicators are the oldest analytical compounds used for acid determinations either titrimetrically or photometrically. They are very sensitive over a narrow acid concentration range which makes them suitable for monitoring low concentrations of the weak organic carboxylic acids. They are not selective, however, and will react with all types of acids as well as bases. A prefilter (a non-volatile acid on a solid support) would be necessary to eliminate interference from the basic amines present in rendering emissions. Volatile inorganic acids and acid gases are not ordinarily encountered in rendering plant operations, so these would not cause a problem except in monitoring at remote distances from the plant exhaust. Laboratory spot tests on paper tape showed that both methyl orange and bromophenol blue, sensitive in the pH 3.0-4.6 range, could measure acetic and propionic acids down to 10 ppm just with visual observation. Sodium fluorescein gave much brighter spots under UV light, but had correspondingly brighter blanks. The acid quenched the fluorescence so that lower concentrations were more difficult to distinguish by eye. Rhodamine 6G, an ester form of the rhodamine dye, is reportedly much more sensitive to organic acids, measuring as little as 0.6 µg of stearic acid. These color or fluorescent indicators, therefore, offered the best possibility for adapting to a tape monitor system.

Phosphomolybdic acid in ethanol is commonly used to develop fatty acid spots on thin layer chromatographic plates. It should work equally well on paper tape since, if necessary, silica gel impregnated tape can be used. It is sensitive to 1 µg or less of saturated fatty acids but the color formed is not very intense and its quantitative characteristics must be investigated.

A third method is the bleaching of the color of ferric-5-nitrosalicylate by water soluble organic acids. The reaction is independent of pH in the range 2.5-3.0, and shows no temperature effect between 10° and 50°C. Moreover, the reagent is stable for over a week. The method, however, has only been tested with dicarboxylic acids; the effect of reducing compounds, such as aldehydes and thiols, was not reported. Mineral acids do not cause bleaching, so this method is potentially specific for organic acids if it is sensitive enough to monocarboxylic acids.

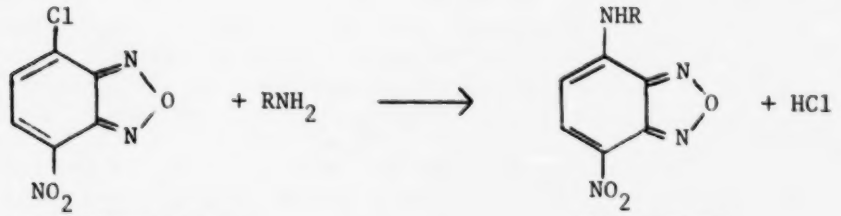
From the methods available for determining amines, two long-standing well-proven methods and a more recently developed one offered the sensitivity and simplicity needed for a field monitor. These were:

(1) NBD (4-chloro-7-nitrobenzofurazan) fluorescence

(2) Dansyl chloride fluorescence

(3) Ninhydrin colorimetric

The NBD chloride method was developed four years ago to determine amino acids and peptides. The compound itself is not fluorescent but its amine derivatives are:



non-fluorescent fluorescent

The compound is quite stable which gives it an advantage over dansyl-chloride. It does not have the background of widespread use that dansyl chloride and ninhydrin have, however, so more work would be necessary to establish the best reaction conditions and eliminate interferences.

Dansyl chloride (1-dimethylamino-naphthalene-5-sulfonyl chloride) is a standard reagent for amines, amino acids, and other amino organic compounds. It has a blue-green fluorescence itself but the amine derivatives fluoresce yellow-green, permitting a clear differentiation although the blank readings are high. Measurement of as little as 50-100 ng of amine compounds have been claimed with the dansyl reaction. It has been used directly on paper chromatograms for the quantitative measurement of separated amino compounds, so it should be directly applicable to tape sampler monitoring. Poor stability of the reagent is its greatest drawback.

Ninhydrin is the classic reagent for the colorimetric determination of amino acids and is commonly used in commercial automatic amino acid analyzers. It is extremely sensitive and is used to develop amino acid spots on paper chromatograms, giving a quantitative measure of the amino acid concentration. If the proper reducing conditions can be achieved to make it react on paper tape with the simple amines, it would be the best colorimetric method for the amines.

The recommended methods for field monitor development are summarized in Table 5.

Table 5 - Class Analysis Methods

Compound Class	Recommended Analytical Methods
Aldehydes:	(1) Reduction of silver ion to silver
	(2) Reduction of Nessler's reagent to mercury
	(3) MBTH colorimetric
	(4) Bisulfite-hydrazine colorimetric
	(5) o-Aminobenzaldehyde and methylamine hydrochloride colorimetric
Acid:	(1) pH color or fluorescent indicator with amine prefilter
	(2) Phosphomolybdic acid colorimetric
	(3) Ferric-5-nitrosalicylate - decolorizing
Amine:	(1) NBD (4-chloro-7-nitrobenzofurazan) fluorescence
	(2) Dansyl chloride fluorescence
	(3) Ninhydrin colorimetric

PHASE II

PROTOTYPE DEVELOPMENTS

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SECTION 4

INTRODUCTION

The prototype development in Phase II was based on modification of standard commercial tape samplers. The ambient air hydrogen sulfide monitor served as the basic instrument for modification to measure each of the three types of odorous compounds found in rendering plant emissions. Originally the program plan called for developing an aldehyde, amine, and an organic acid monitor. These were reportedly the three most odorous types of compounds resulting from meat rendering. The analytical work in Phase I of the project, however, disclosed that more organic sulfur compounds than organic acids appeared in the rendering plant emissions. This, coupled with the much more repulsive nature of the odor of volatile thiols and sulfides, led to the decision to replace the organic acid monitor with an organic sulfur monitor.

Laboratory tests with different Whatman papers available in tape form led to the selection of Whatman No. 1 paper for the aldehyde and amine monitors and No. 54SFC for the organic sulfur monitor. Of the papers tested, numbers 3MM, 40, 120, and 541 had very high aldehyde blanks (greater than 10,000 ppm aldehyde), while numbers 1, 20, and 540 had acceptable but still moderately high blanks. Amine blanks for these papers were all low with number 1 the lowest, making it the best choice for both aldehydes and amines. While number 54SFC gave the best reagent blank for sulfur, all the papers developed a very high blank for the sulfur determination when they were stored for a few hours at room temperature after being impregnated with reagent.

Spot tests on the paper tapes with the different reagents selected for each compound class eliminated the methods least suited to tape monitoring analysis. Table 6 summarizes the results. The sample solutions for these tests ranged from 0.01 to 1000 ppm in concentration. The results clearly indicated the superiority of MBTH for aldehydes and ninhydrin for amines, and the greater practicality of determining the sulfur compounds as SO_2.

Selection of these analytical methods meant that the basic tape samplers for aldehydes and amines required the addition of reagent heads, blank (background) reading heads, reagent pumps, and interval timers for the automatic analysis. The organic sulfur monitor, in which the sulfur compounds are first thermally oxidized to SO_2 which then reacts with reagent added to the tape, required a reagent addition system, oxidizer furnace, and a bubbler to provide water vapor for the reaction. In their final design, all three instruments performed repetitive sampling and analysis automatically with continuous strip chart recording readout.

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Table 6 - Evaluation of Analytical Methods

Compound Class	Method*	Tape Spot Test Results
Aldehydes	Silver ion	Reagent unstable on tape
	Nesslers	Reagent unstable on tape
	MBTH	Moderate blank, stable, sensitive
	Bisulfite	Not sensitive enough
	Benzaldehyde	Unstable
Amine	NBD	Unstable
	Dansyl	High blank on tape
	Ninhydrin	Low blank, high sensitivity
Sulfur	H_2S	Requires complete reduction of air sample
	SO_2	Requires oxidation of organic compounds

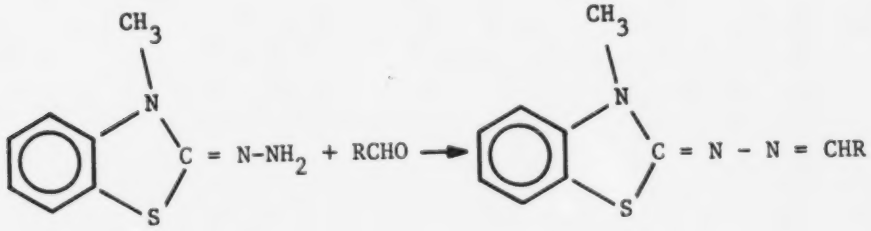
*See Table 5

SECTION 5

ALDEHYDE MONITOR

5.1 ANALYTICAL METHOD

In the aldehyde monitor, 3-methyl-2-benzothiazolone hydrazone (MBTH) in the paper tape selectively collected the aldehydes from the sample air. Addition of acid ferric chloride solution developed a characteristic blue color related in intensity to the concentration of aldehyde. The reaction is well established for analytical use and is the method selected by the Intersociety Committee for determining formaldehyde.[5] The aldehyde reacts with MBTH by a condensation reaction:



The ferric chloride oxidizes excess reagent which couples with the aldehyde product giving the dark blue compound.

Formaldehyde produces the most intense color with the MBTH method, but other volatile aldehydes also react producing the same blue color. The method, therefore, can serve for class analysis of volatile aldehydes.

Heating speeds the color development on the tape, 100°C giving maximum color in 2 min, but also increases the blank. A high blank reduces the sensitivity of the color intensity measurement by excluding too much light from the measuring photocells, so the monitor procedure was based on room temperature color development.

The impregnating solution for the paper tape consisted of 1.0g 3-methyl-2-benzothiazolonehydrazone·HCℓ dissolved in 1000 ml distilled water and filtered through No. 40 Whatman filter paper. The color-developing acid ferric chloride solution contained 1.6g sulfamic acid (analytical grade) and 1.0g $FeCl_3$ dissolved in 100 ml distilled water and filtered through No. 40 Whatman filter paper.

5.2 TAPE MONITOR DESIGN

The additional reading and reagent addition heads fit in-line on the front panel of the basic tape sampler after moving the tape storage canister, sampling head, and the attendant tape guide spindles to the left. Figure 8 outlines the position of these components on the front of the instrument. The panel width of this particular sampler permitted matching the spacing between the heads to the tape advance distance. This eliminated any need to modify the tape advance system in the instrument.

The first design for the aldehyde monitor required only addition of the extra heads, a reagent addition metering pump, and rewiring of the timer circuit. It relied on metered addition of reagent from a center feed reagent head [Figure 9(a)]. Capillary action would draw the acid ferric chloride rapidly onto the tape as soon as the solution column touched the bottom of the tape. This would drain all the solution from the center feed plug and horizontal connecting channel in the head. A peristalic pump, triggered by the sample timer, would refill the reagent head channels with solution during the first tape advance. Attempts to synchronize the filling rate with the tape transport proved futile, however, and this simple design had to be replaced with one using a separate interval timer to control the analytical steps.

In the second design, the additional interval timer, allowed full initial tape advance before starting the reagent addition pump. It also permitted individual adjustment of both pump operating time and total reagent addition interval time before the second tape advance. This eliminated the impractical synchronization requirement of the first design but confirmed two other problems in reagent addition. The first was the radial transport of developed aldehyde color by the flow of reagent from the center feed point. A colored ring formed, instead of a color spot, leaving a largely clear center area. The high light transmission of the colored ring reduced the measurement sensitivity. Moreover, even slight spreading of the ring outside the light area of the reading head caused a large error in the opacity reading. The second problem was variation in the amount of reagent drawn from the reagent head by the capillary action in the paper tape. The tape would sometimes pull reagent from the connecting tubing to the head, so that the amount of reagent added by the pump during the next analytical cycle was not enough to fill the head and reach the tape.

A small cup reservoir in the center of the reagent head, Figure 9(b), did not eliminate the variations in reagent addition. Capillary action in the centerfeed channel still carried reagent from the connecting tubing to the cup as reagent flowed onto the tape. Changing to an annular reservoir, Figure 9(c), improved the spot formation by introducing bi-directional reagent flow in the tape. The reagent, however, usually wet the tape first just above the feed channel causing an off-center spot. Chamferring the inner edge of the annular reservoir [Figure 9(d)]

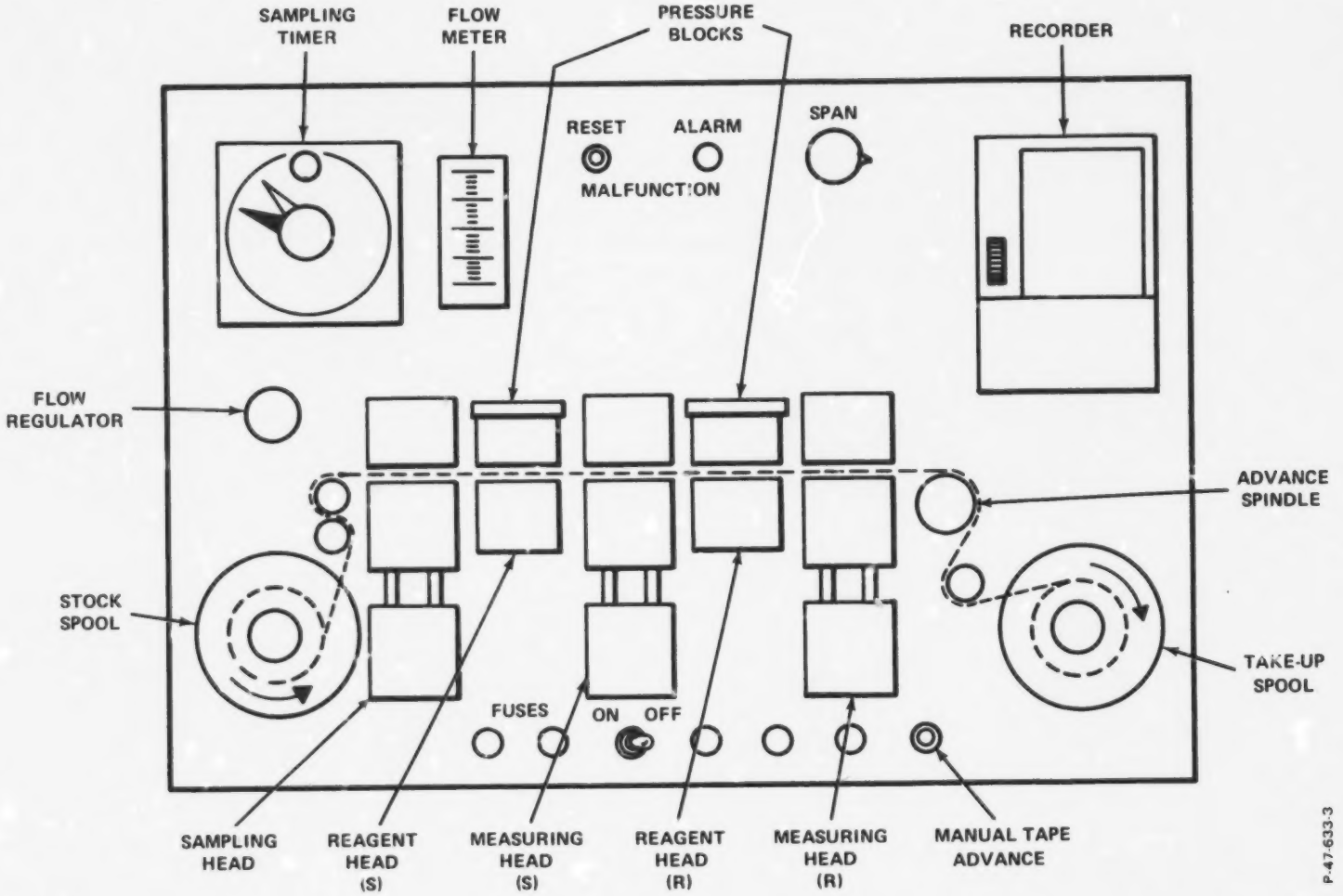


Figure 8 - Front Panel Components

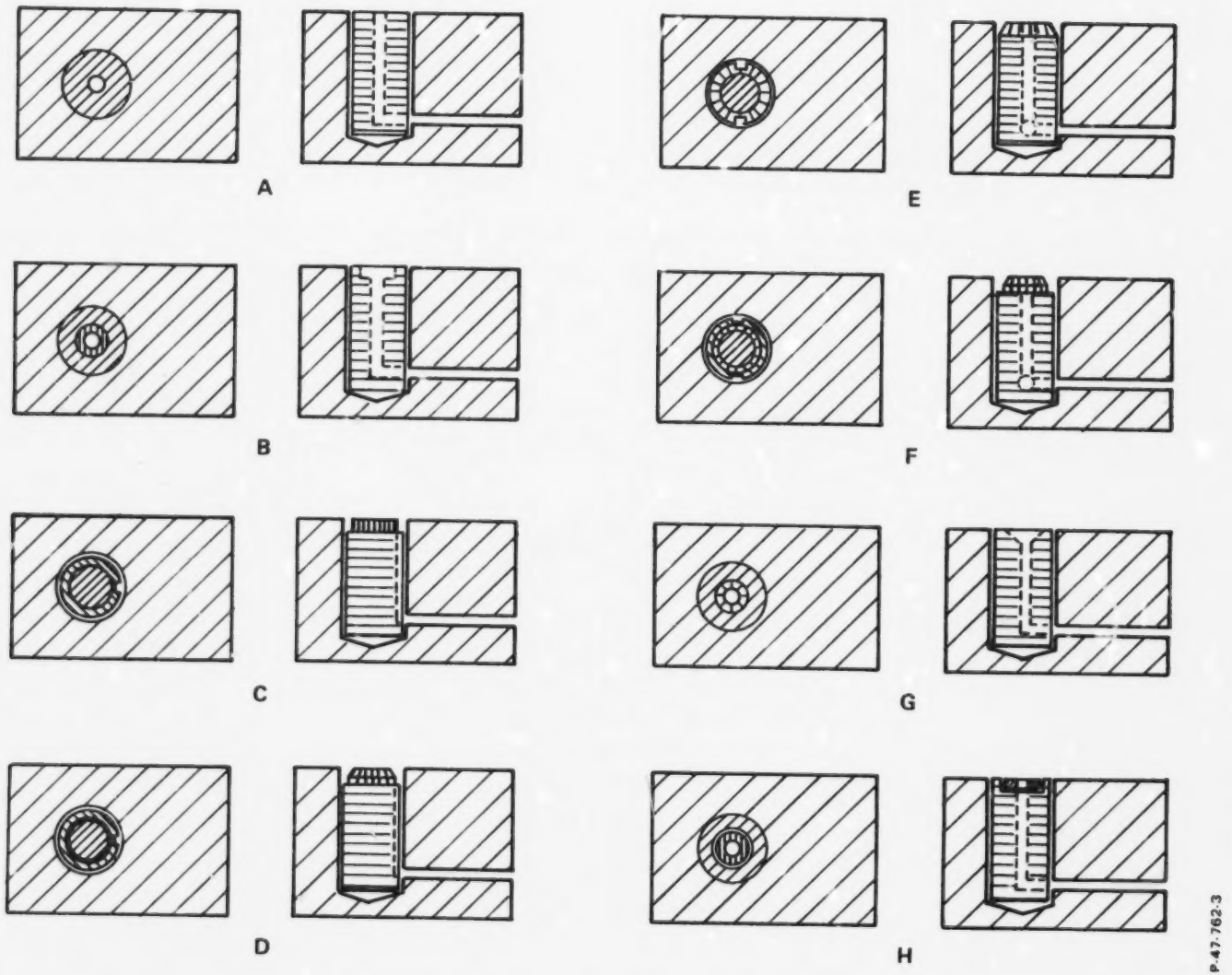


Figure 9 - Reagent Addition Heads

reduced this tendency somewhat but did not eliminate it. Attempts to fill the annular reservoir through two feed channels were not successful with either a completely beveled [Figure 9(e)] or chamferred [Figure 9(f)] inner edge. The tape would usually wet first above one or the other feed channel leading to an off-center spot. Packing the reservoir with fine glass wool gave uniform wetting around the reservoir as long as the glass wool stayed wet with reagent. When the reagent dried in the reservoir during sampling, however, the next reagent addition was always off-center.

Adding the reagent as a drop from above spread the spot into a ring extending beyond the transmission area of the reading head. About one-third to one-half a drop (0.02 - 0.03 ml) gave the best spot size. For the final design, therefore, it was necessary to return to the center feed head. Introducing a Teflon center plug with a funnel-shaped cup [Figure 9(g)] decreased the capillary action in the feed channel making the volume of reagent added more uniform. Occasional variations in flow volume still occurred leading to a missing spot in the next analysis cycle. Placing a Teflon "washer" into a cup-shaped reservoir [Figure 9(h)] reduced the possibility of missing additions still further by providing three or four small pulse additions of reagent as the pump added reagent to the cup. This type of reagent head was used in the final prototype design.

Individual pumping to each reagent head proved necessary to eliminate preferential flow into the head which first wet the tape. A peristaltic pump with two feed tubes was satisfactory except for the periodic low volume addition when a pump roller lifted from the tubing. A syringe pump (Sage Model 341) modified to hold two 10 ml syringes eliminated this problem. Plastic, disposable syringes proved unsatisfactory, however, because their sliding rubber seals showed stick-slip action along the barrel. This caused delayed addition of reagent with the tape wetting, at times, during or after its second advance. Glass syringes gave smooth uniform addition of reagent to the head. Thorough greasing with a hydrocarbon or silicone grease prevented "freezing" of the syringe through drying of reagent solution between the barrel and plunger.

The ring nature of the developed aldehyde spot, illustrated in Figure 10, led to two additional changes in the reading heads. Blocking the center portion of the opening to the photocell chamber below the tape eliminated a large part of the excess light transmitted by the colorless, eluted center area of the spot. The circular area blocked was 14 mm in diameter, leaving a 4 mm wide annular reading zone for light from the upper chamber to pass through the tape and into the lower photocell chamber. The photoconductive cell was then replaced with one of larger diameter located at the bottom of the chamber to intercept more of the light from the annular reading zone.

The electronic circuit of the tape sampler was not modified. The sample photoconductor cell controlled the inverse input to an operational amplifier as shown in Figure 11 so the output reading increased

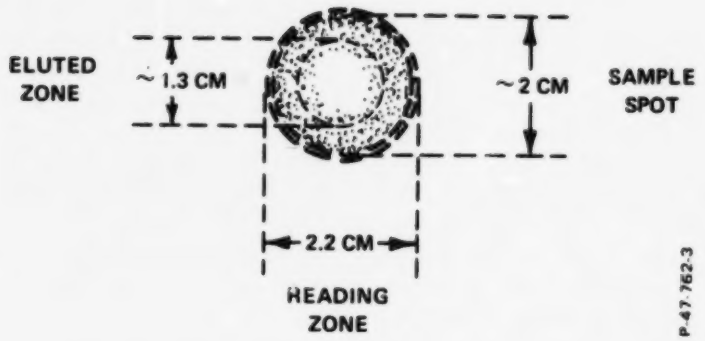


Figure 10 - Aldehyde-MBTH Spot Geometry

with increasing opacity of the sample spot. The electrical wiring was changed to accommodate the interval timer as shown in Figure 12 along with the syringe pump and extra reading heads. Detailed wiring diagrams appear in the Operating Manuals provided with the instruments.

The final design for the front panel of the monitor is shown in Figure 8. The reagent heads were polycarbonate plastic with blocks of the same material pressing the tape against their delivery surface. The sampling head collected a 1.5 cm diameter spot while the reading heads measured a 2.2 cm diameter area. Figure 13 shows the position of the analysis components inside the monitor. The photograph in Figure 14 shows these components in place with the syringe pump mounted on top of the sampling pump. Figure 15 shows the monitor in its case but with the front cover removed.

5.3 LABORATORY TESTS

Both ethanal (acetaldehyde) and methanal (formaldehyde) were used in preliminary tests with MBTH-impregnated tape. Once spot formation and color development was established, aqueous methanal solutions proved most convenient for evaluating design modifications in the monitor. Solutions of less than 1% methanal in water have the same vapor and liquid composition,[7] so that parts per million (ppm) solutions in a bubbler provide a convenient source of methanal at fixed concentration. Sampling times of 3 to 4 min were adequate for repetitive tests with a 350 ppm methanal solution in water. A standard 25 ml midget impinger containing 10-15 ml of the solution was connected to the input of the monitor sampling head with a short length of polyvinyl chloride tubing (Tygon tubing). With the monitor flow control set to draw room air through the bubbler and tape at 0.5 or 1 ℓ/min (1 or 2 CFH), an increase in spot color intensity was clearly visible by eye after 3 min sampling. The room air alone did not produce a visible change in spot color.

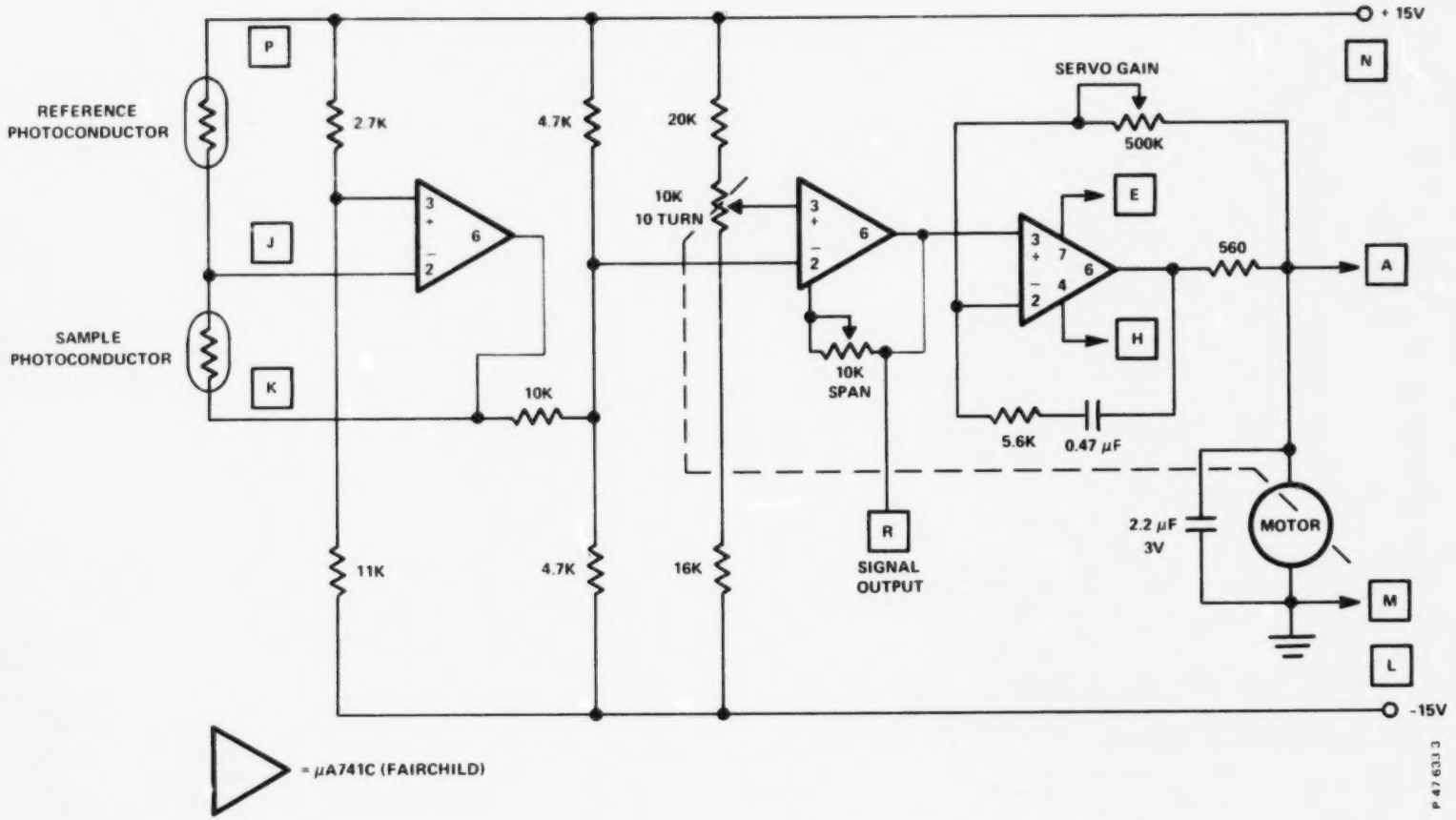


Figure 11 - Amplifier and Automatic Zero

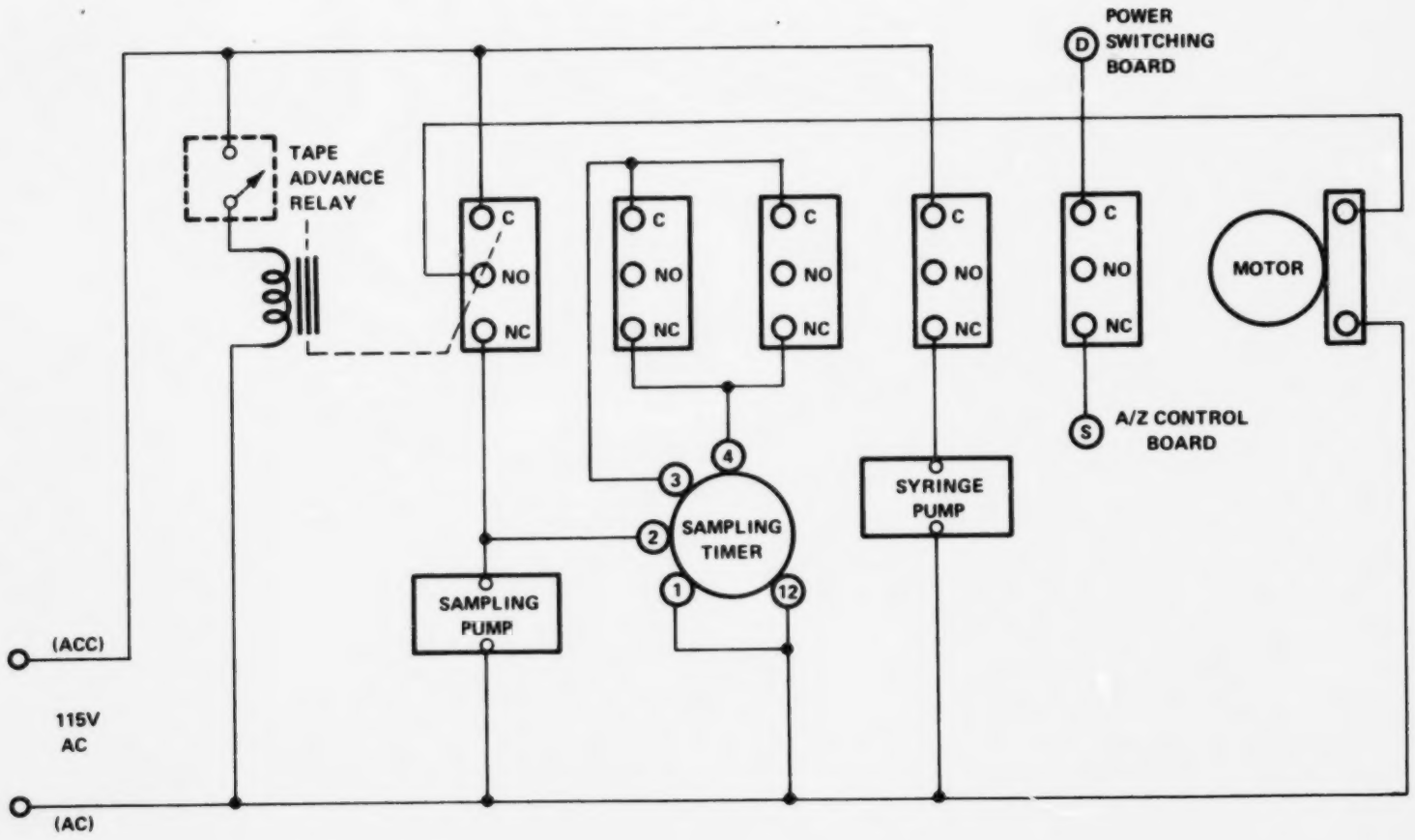


Figure 12 - Interval Timer Circuit

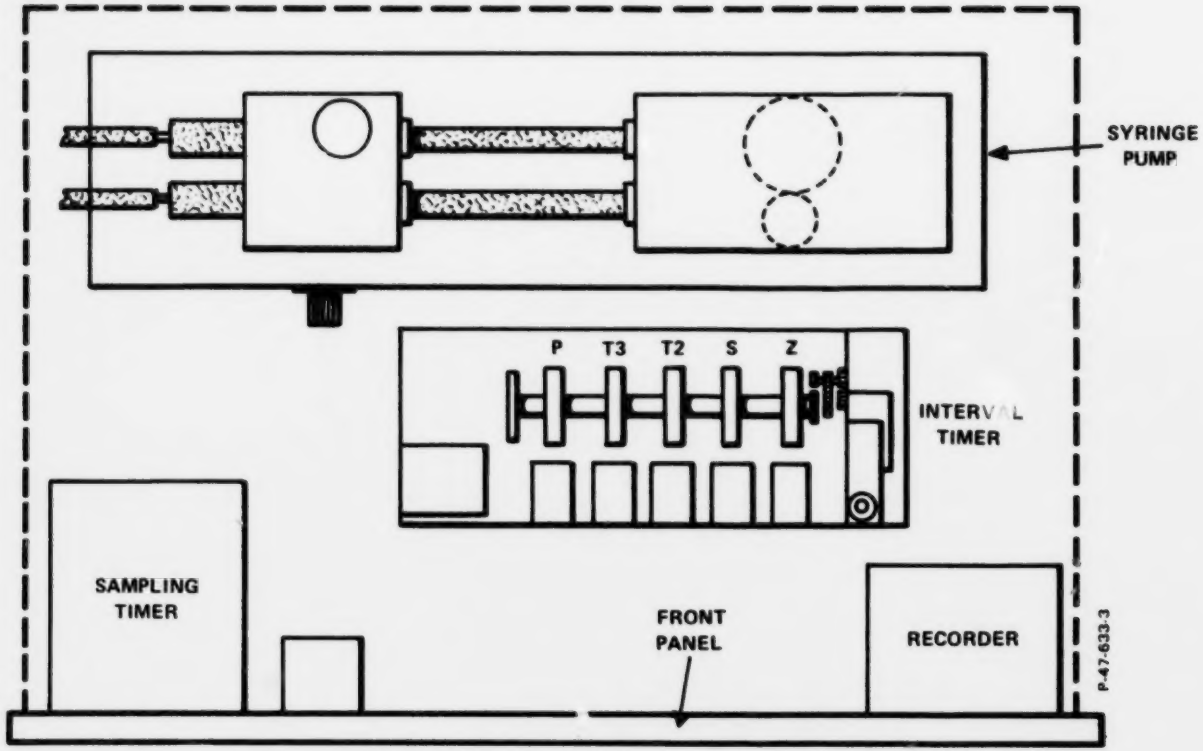


Figure 13 - Internal Analysis Components

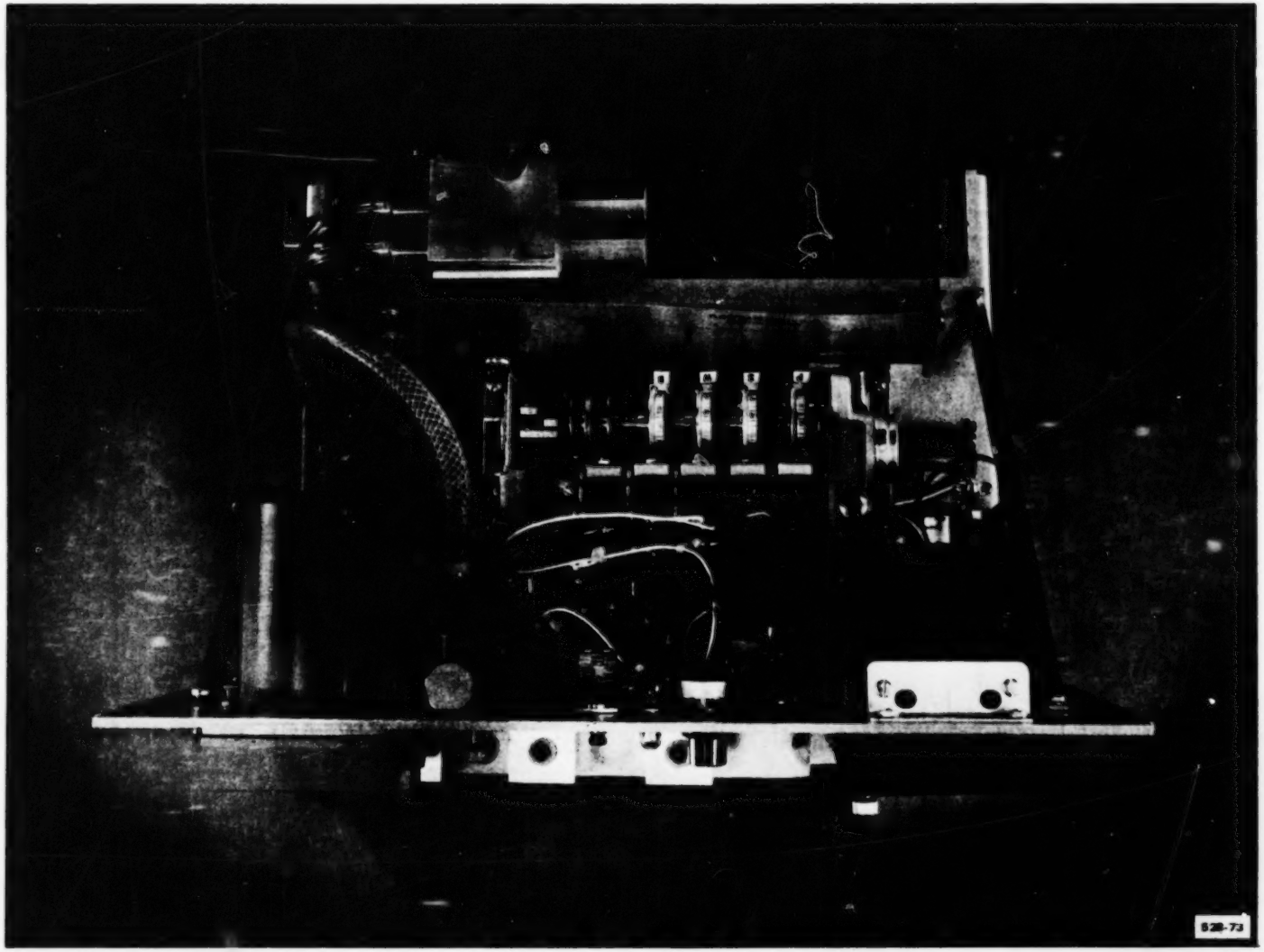


Figure 14 - Analysis Components with Mounted Syringe Pump

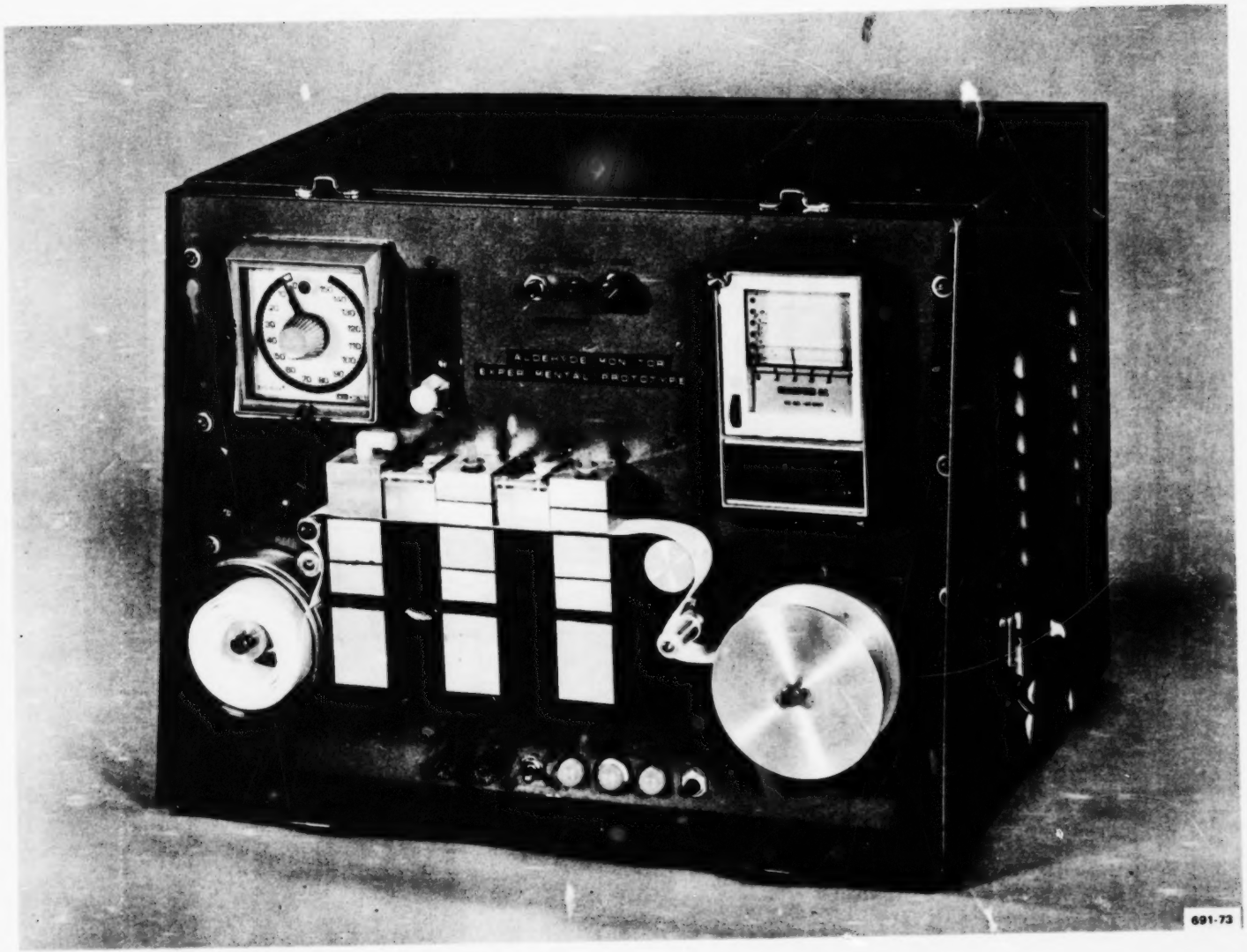


Figure 15 - Aldehyde Monitor in Case (front cover removed)

The analytical cycle shown in Figure 16 was used in operational tests of the monitor. The sampling timer triggered the initial tape advance at the end of the sampling period. This activated the interval timer which automatically controlled the analytical cycle. The sampling pump turned off immediately as the tape heads opened for the first tape advance to the reagent addition position. The tape spot that was in the first (sample) reading head moved to the right hand reagent head to become the blank spot for the reference head. For most tests, the reagent syringe pump stayed on 9 s with a delivery speed of 0.19 ml/min. This would transfer 0.03 ml of acid ferric chloride solution to the reagent head and tape. The tape then advanced to the reading position where it stayed for 87 s for recording of the color development. The final tape advance brought fresh tape into the sample and reading heads; at the same time, the interval timer activated the automatic zero circuit.

The recorder plotted continuously giving a record of blank tape opacity during the sampling period and the difference in blank and sample spot color development after reagent addition. The tape transport and reagent addition steps, being of short duration compared to sampling and reading, gave scattered points on the recorder chart. Sample recordings are illustrated in Figure 17. The straight, continuous vertical lines represent the sampling period preceded by the automatic zero adjust. The horizontal dotted lines, converging toward a continuum, show the spot color development. If the sample and reference spots developed the same geometrically, the recorded points converged toward a higher opacity reading as the sample spot became darker than the reference spot. A slight difference in the development of the spots caused the opacity readings to converge toward a lower reading as occurred in the last run

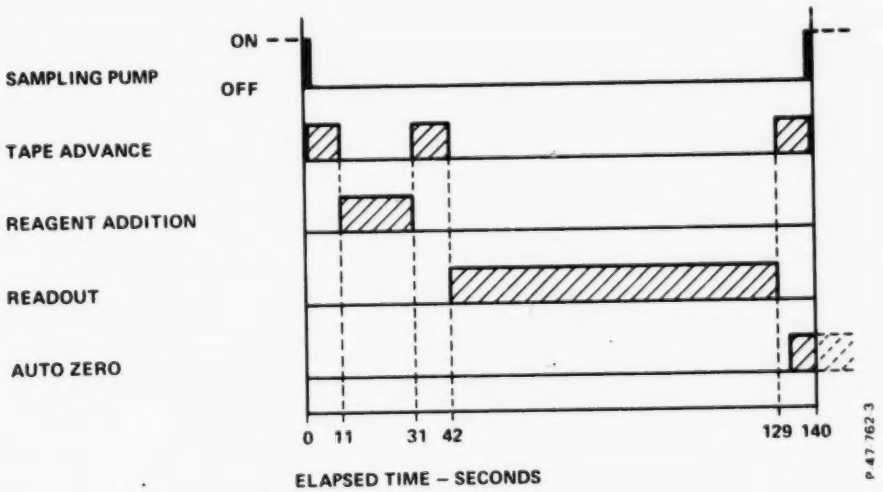


Figure 16 - Aldehyde Analytical Cycle

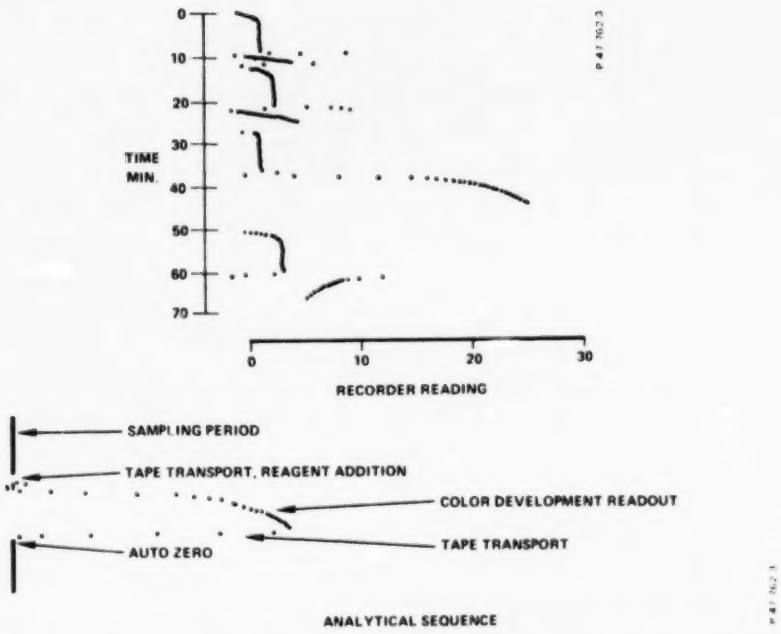


Figure 17 - Recorder Plots During Sampling and Analysis

shown in Figure 17. A large difference in spot diameter or elution pattern caused erratic or off-scale opacity readings.

The experimental work with different reagent addition heads led to a design that produced reasonably uniform spot diameters. It was then possible to compare recorder opacity readings with reference and sample spot diameters. Test results, such as those plotted in Figure 18 showed that with differences of 0.5 cm or less in sample and reference spot sizes, the spot size did not control the recorder reading. As the individual spot diameters plotted at the top show, none of the spots exceeded the 2.2-cm diameter reading zone. The pattern of the recorder readings, however, showed no correlation with either the sample or reference spot diameters nor with their difference. The only other variable in the color spots was the elution pattern which formed as the reagent flowed onto the tape from the center feed in the head.

Blocking the light passing through the center, mostly colorless portion of the spots so that only a 4 mm wide annular zone affected the light transmission proved to be an effective, short-term solution to the extreme variations in opacity readings. With this center stop in place, none of the readings in 37 consecutive runs exceeded 26. While these annular zone readings were more sensitive to spot diameter, they eliminated the very high opacity readings (for low aldehyde concentration) caused by the greater transmission of the center, colorless part of the reference spot compared to that of the sample spot. This made

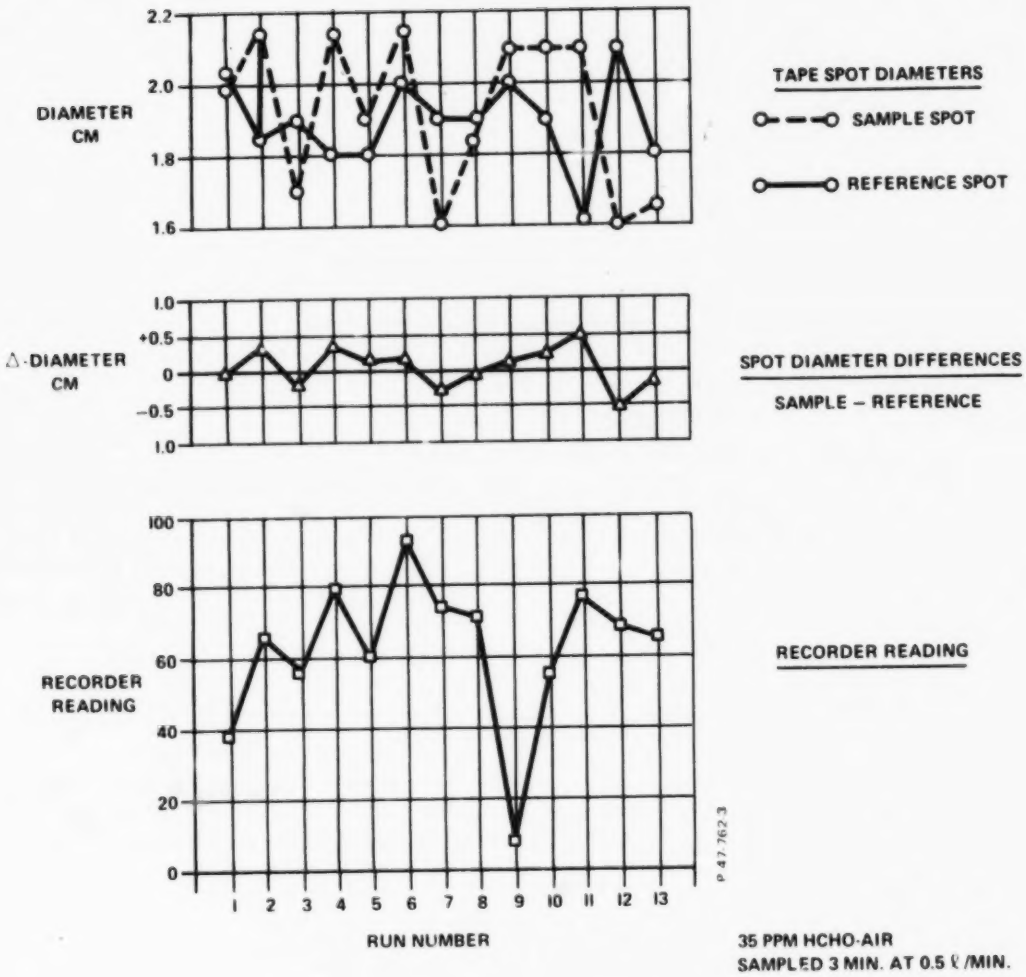


Figure 18 - Variation in Aldehyde Reading and Spot Diameters

it possible, then, to record the presence of high aldehyde concentrations in a sequence of runs without serious interference from wayward readings. Measurements at a rendering plant, compared to laboratory runs discussed in Section 6, confirmed this.

SECTION 6

AMINE MONITOR

6.1 ANALYTICAL METHOD

The classic ninhydrin colorimetric method for amino acids proved best in preliminary experiments for amine analysis on tape strips. Reagent stability and color development temperature posed the two major problems of immediate concern in adapting the method for a tape monitor. Impregnating the tape with only the sodium acetate/acetic acid buffer gave a very stable tape with enough acidity (pH 5.5) to collect amine compounds. The ninhydrin/stannous chloride color-developing solution made in 2-methoxyethanol (Methyl Cellosolve) was stable for over three days at room temperature and under ambient light.

The solutions finally used in the tape monitor method consisted of a tape-impregnating buffer containing 270g of sodium acetate trihydrate and about 50 ml of glacial acetic acid in 500 ml of distilled water (final pH adjusted to 5.5 $\pm$ 0.1), and a color reagent of 2.0g ninhydrin and 0.5g stannous chloride in 100 ml of 2-methoxyethanol (Methyl Cellosolve). This combination gives a very sensitive measure of amine compounds as a class. Color development is slow at room temperature, but experiments with heating the tape to speed the reaction showed an undesirable increase in the blank color above 40°C. To avoid the increased blank and the undesirable complexities of controlled heating for the tape, the final procedure was based on ambient temperature color development with a four-minute color development period.

6.2 TAPE MONITOR DESIGN

The amine tape monitor required the same analytical steps as the aldehyde monitor, so its physical design was essentially the same. The solvent-penetrating action of 2-methoxyethanol made it incompatible with polycarbonate and most other plastics useful as reagent head materials. In addition, its low surface tension caused it to creep over the surface of ordinary structural plastics. Only Teflon met both the physical and chemical requirements for delivering the 2-methoxyethanol reagent solution.

The combined low surface tension and low density of the reagent solution simplified the choice of reagent head design. Its weaker capillary action made its flow rate in the tape much slower than that of the aqueous aldehyde reagent. As a result, the elution effect was much smaller and the color spots were more uniform. The straight centerfeed channel [Figure 9(a)] still gave erratic feeding, however, by occasionally carrying some reagent out of the delivery tube during reagent addition. This meant that there was not enough reagent to completely fill the reagent head channels during the next addition period, thus resulting in a missed

spot. The funnel-shaped cup design [Figure 9(g)] finally proved satisfactory so the reagent heads were made of solid Teflon with a delivery channel of this shape.

The sampling, reagent addition, and reading heads had the same positions as on the aldehyde monitor (Figure 8) with a 1.5 cm sampling spot diameter and 2.2 cm diameter measuring areas. The uniformity of the spots eliminated any need to block out their center portion for transmission measurement. The reagent syringe pump and the interval timer occupied the same positions shown in Figures 13 and 14. The amine analysis cycle required different time intervals and these are shown in Figure 19. Again, the electronic circuit was not changed; only the electrical connections were changed to accommodate the pump, interval timer, and additional reading heads as shown in Figure 12. The front panel of the monitor, with its cover removed, is shown in Figure 20.

6.3 LABORATORY TESTS

Operation of the prototype model was tested in the laboratory with both monomethylamine and propylamine. The acetate buffer tape collected the amines readily at air sample flows of 0.5 and 1 ℓ/min. Experiments with different reagent addition head designs showed that using excess reagent to completely flood the sample spot produced more reproducible opacity measurements than precisely metered reagent addition. The flow of reagent in the tape paper is irregular and forms unsymmetrical spots. Flooding with reagent gives a large color spot exceeding the reading head area, but the collected amines react in place. Since the eluting

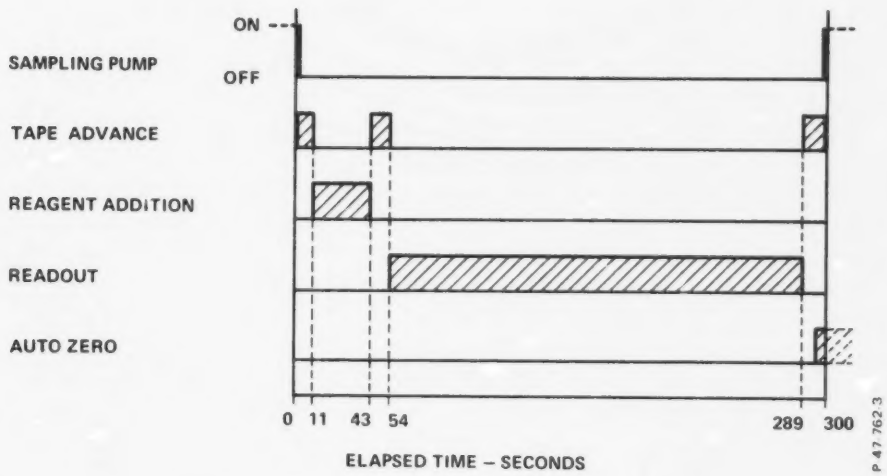


Figure 19 - Amine Analytical Cycle

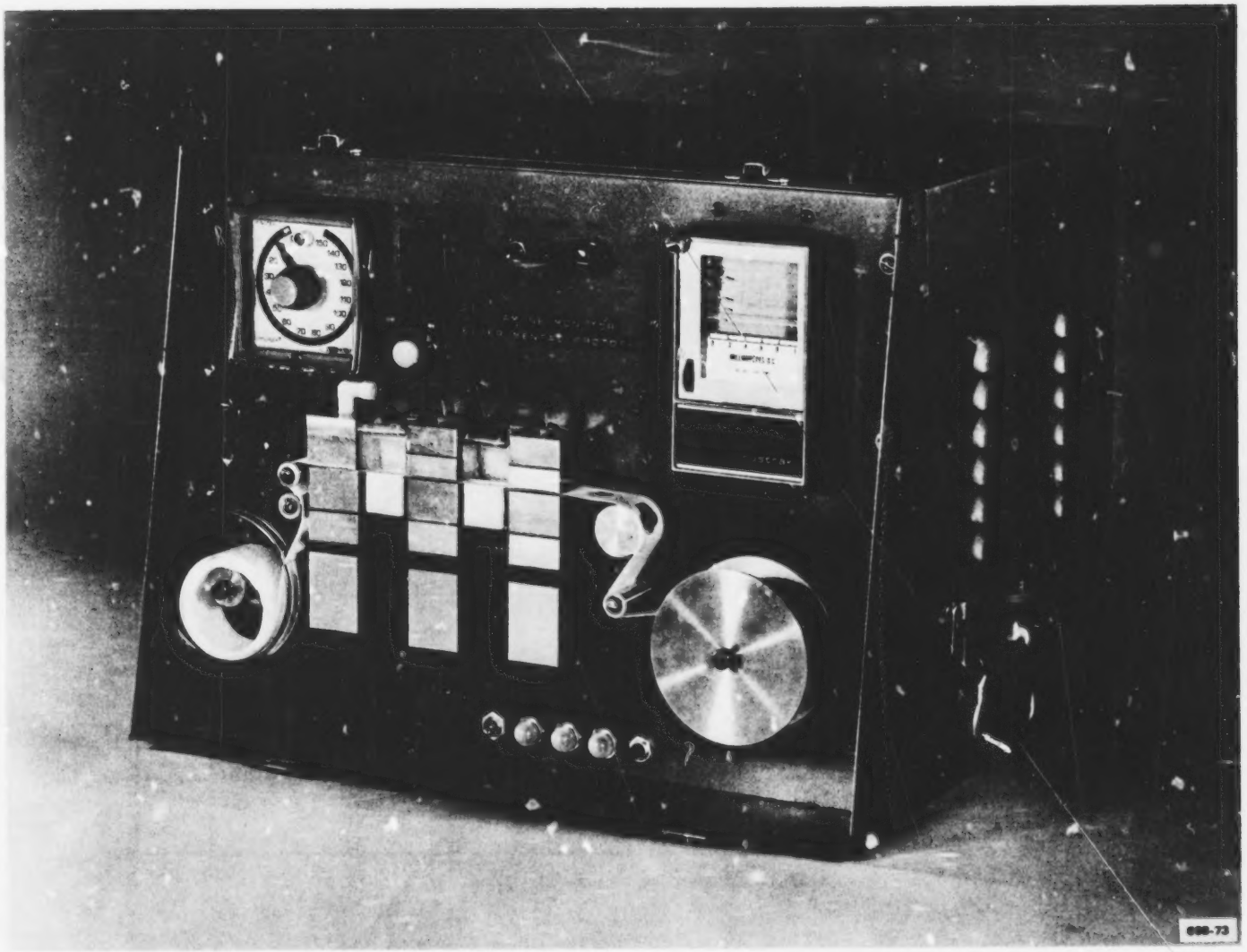


Figure 20 - Front Panel of Amine Monitor (cover removed)

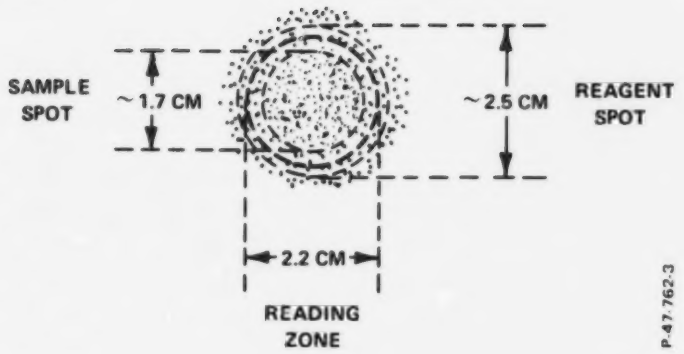


Figure 21 - Amine-Ninhydrin Spot Geometry

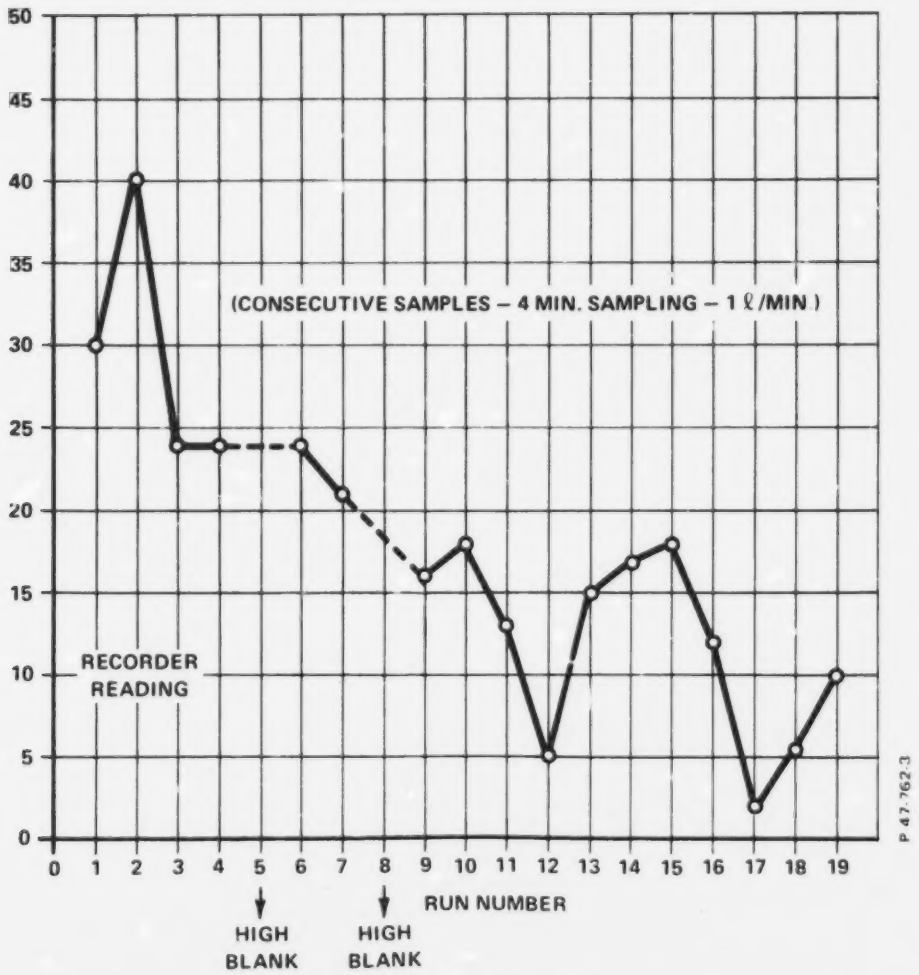


Figure 22 - Amine Monitor - Depletion of Amine from 1000 ppm Propylamine Aqueous Solution

action of the flowing reagent is small, the amines form a darker sample spot inside the large reagent spot, thus giving a more reproducible background color. This is illustrated in Figure 21.

The chart recording of the sampling and analysis runs was similar to that for the aldehyde monitor (Figure 17) except for the longer measurement time. Recorded measurements converging toward lower opacity readings were more common with the amine analyzer, and the readings sometimes reached a constant value near the end of the measurement period. Reproducibility of readings was very good for a tape spot measurement. A series of blank runs, made for comparison with test runs at a rendering plant, gave recorder readings ranging from 1 to 7.5 with an average of 4 and a standard deviation of 1.8. Sequential readings on air bubbled through an aqueous solution initially containing 1000 ppm propylamine clearly recorded the loss of amine from the solution. Figure 22 shows the plot of these readings. High blanks, that is, blank spots more dense than the sample spots gave below zero readings for samples 5 and 8. These results indicated that the instrument could monitor amine emissions for either sudden changes or long-term drifts in concentration.

SECTION 7

ORGANIC SULFUR MONITOR

7.1 ANALYTICAL METHOD

The presence of several different types of malodorous organic sulfur compounds in the rendering plant emissions dictated the choice of a total sulfur analysis instead of analysis for a single class or a specific compound. The total sulfur analysis would also include any sulfur dioxide or hydrogen sulfide, although these are not common to rendering emissions. Oxidation of the organic compounds in the emissions sample followed by complete reduction of all the sulfur compounds to H_2S would provide a sample for direct measurement on existing H_2S tape monitors. The reduction, however, would require continuous reaction of all the oxygen and oxidized compounds in the flowing sample gas with excess reducing agent. The need for a continuous supply of reducing gas, such as hydrogen, would effectively make the monitor a fixed position instrument, instead of portable, and would add considerably to its cost. Modifying a tape monitor to collect and measure SO_2 provided a simpler solution to the problem.

Common methods of analysis for SO_2 involve oxidation-reduction reactions measured titrimetrically (starch-iodide) or coulometrically (iodide or bromide) and were not suitable for adaptation to a tape monitor. Colorimetric methods based on fuschin or rosaniline (the West-Gaeke method, for example) are too complicated and technique-sensitive for automation on a tape monitor. One of the most direct and simple colorimetric methods for SO_2 involves reaction with ferric ammonium sulfate to form ferrous ions which give a deep pink-orange color with 1,10-phenanthroline. This is also one of the most sensitive methods, giving a measurable color with less than 100 ng of SO_2. The two compounds are stable and compatible so they can be mixed and added to the tape as one reagent which develops a color as SO_2 is absorbed. This method was chosen, therefore, to measure the total sulfur as SO_2 after thermal oxidation of the sample.

Copper oxide wire pellets packed in a quartz tube and heated to 600°C in a small resistance-wire furnace served as the oxidizer. The absorbing-measuring solution contained 0.2g $FeNH_4(SO_4)_2 \cdot 12\ H_2O$, 0.65g 1,10-phenanthroline, and 40 ml glycerol in 65 ml of 1:1 methanol-water. The glycerol acted as a hygroscopic agent to help provide water for the reduction reaction. SO_2 absorption and reaction take place at the same time in tape wetted with the reagent solution.

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7.2 TAPE MONITOR DESIGN

The combined absorption-reaction property of the SO_2 reagent permitted modifying the basic tape monitor for continuous recording of the color development as the oxidized sample gas passed through the tape. The reagent addition head was placed just before the combined sampling measuring head. Gravity feed was adequate in delivering enough reagent during the tape advance to flood the tape. This assured that the portion of the tape held in the sampling-measuring head during the collection period was saturated with reagent. Using mixed methanol-water instead of just water for the reagent solution avoided weakening the paper tape so much that the air flow would tear it in the sampling head.

The need to assure adequate water for the SO_2 oxidation in the tape made an auxiliary moist air supply necessary. This consisted of a bubbler with a fritted-glass gas dispersion tube immersed in distilled water in a polyethylene bottle. Filtered exhaust air from the sampling pump passed through the bubbler and joined the sample gas stream at the entrance to the sampling head. A valve and flowmeter in this recirculating air line gave the necessary control and flow reading so the sample flow could be set as the difference between the total flow and the recirculated flow. Figure 23 shows diagrammatically the complete analytical train including the reagent addition system. Connecting lines were all Teflon tubing with appropriate Teflon or polyethylene fittings.

The mixed reagent, stored in a vented-cap polyethylene bottle clamped near the top of the front panel inside the instrument, flowed by gravity down through an all-Teflon solenoid actuated valve (Angar Scientific Corp. 190P12) then through a glass-Teflon needle valve and into the reagent head. The switching circuit that automatically opened the tape head during tape advance also opened the reagent valve to let reagent flood the tape as it advanced. A manual push button switch allowed opening the reagent valve for preliminary flow adjustment or to drain the reservoir.

Figure 24 shows the components inside the instrument with an identifying diagram in Figure 25. A transformer mounted on the hinged chassis cover provided 55 V AC for the heating elements in the oxidation furnace. Operating the furance under steady state conditions eliminated the need for temperature-controlling circuitry; using 55 V on the heating elements, rated for 120 V, assured extended life under continuous operating conditions. The front panel components, shown in Figure 26 and identified in Figure 27 were essentially the same as those used for the aldehyde and amine monitors. The reagent head was the simple centerfeed design, Figure 9(a), made from polycarbonate plastic. A polished plastic block clamped under gentle spring tension held the tape against the reagent to assure contact and even flow of the reagent. With the bubbler flow set for 1400 ml/min and the total flow for 2000-2600 ml/min, giving sample flows of 600-1200 ml/min, the monitor would automatically collect

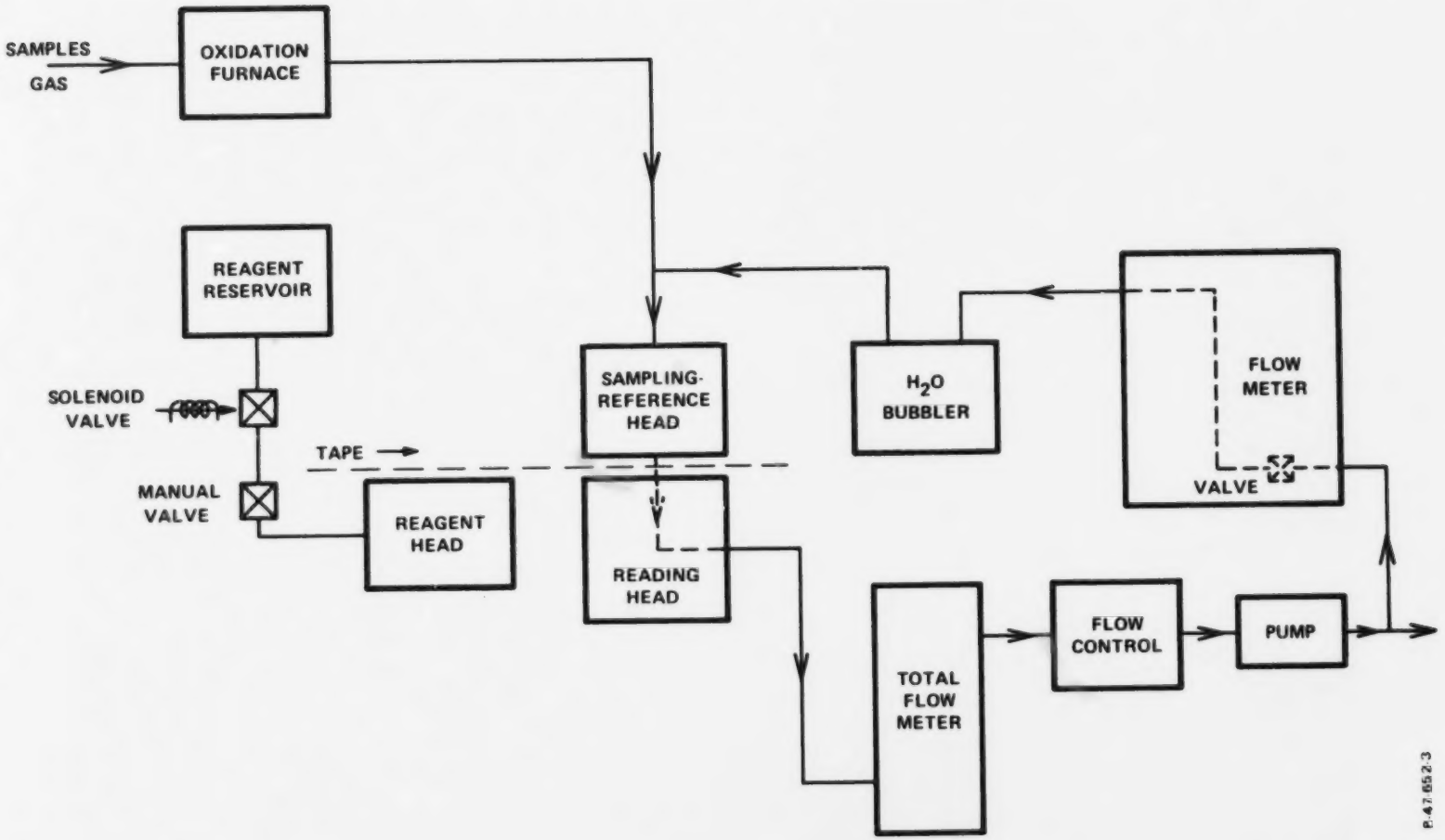

Figure 23 - Organic Sulfur Monitor - Sampling System

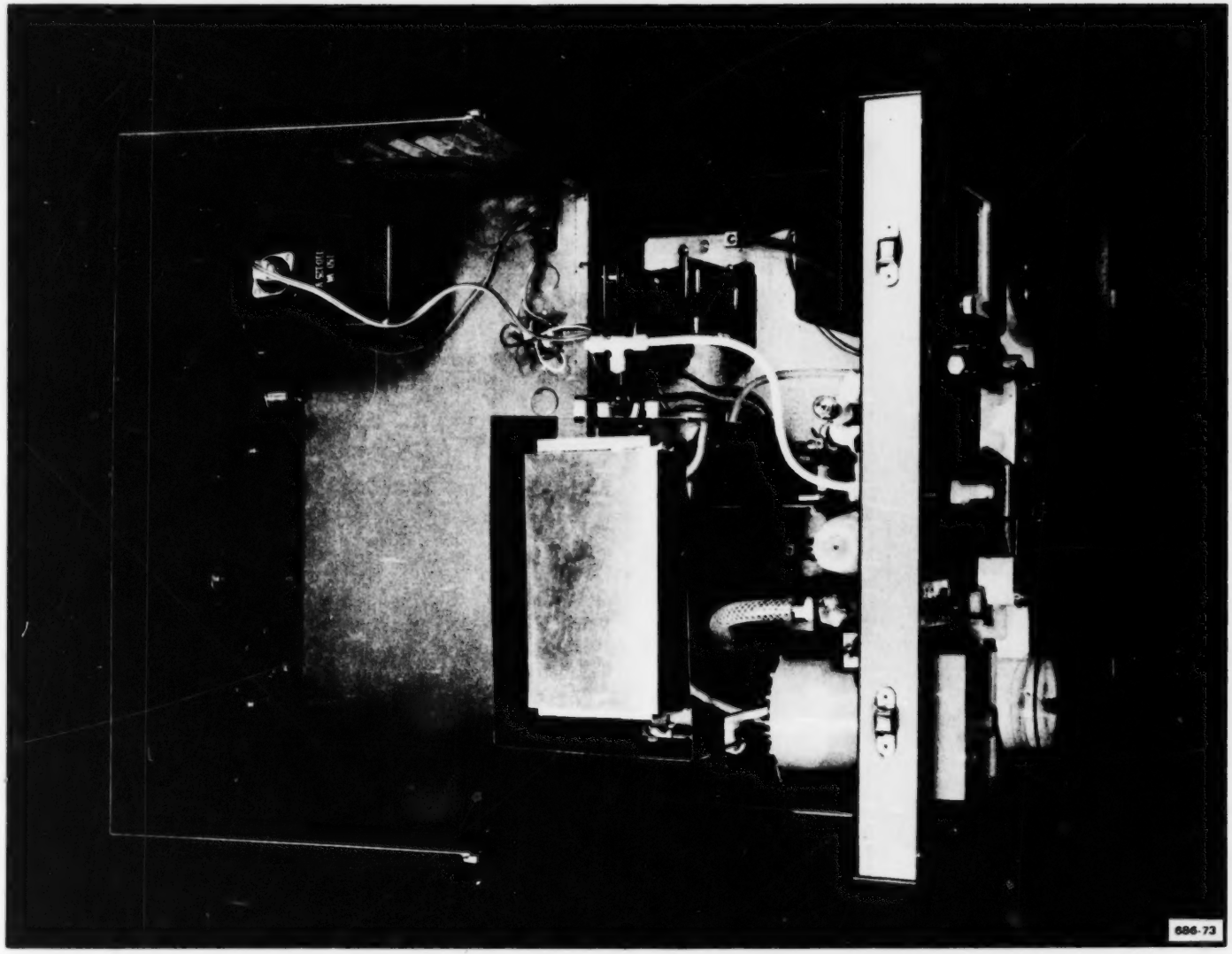

Figure 24 - Organic Sulfur Monitor - Sampling System

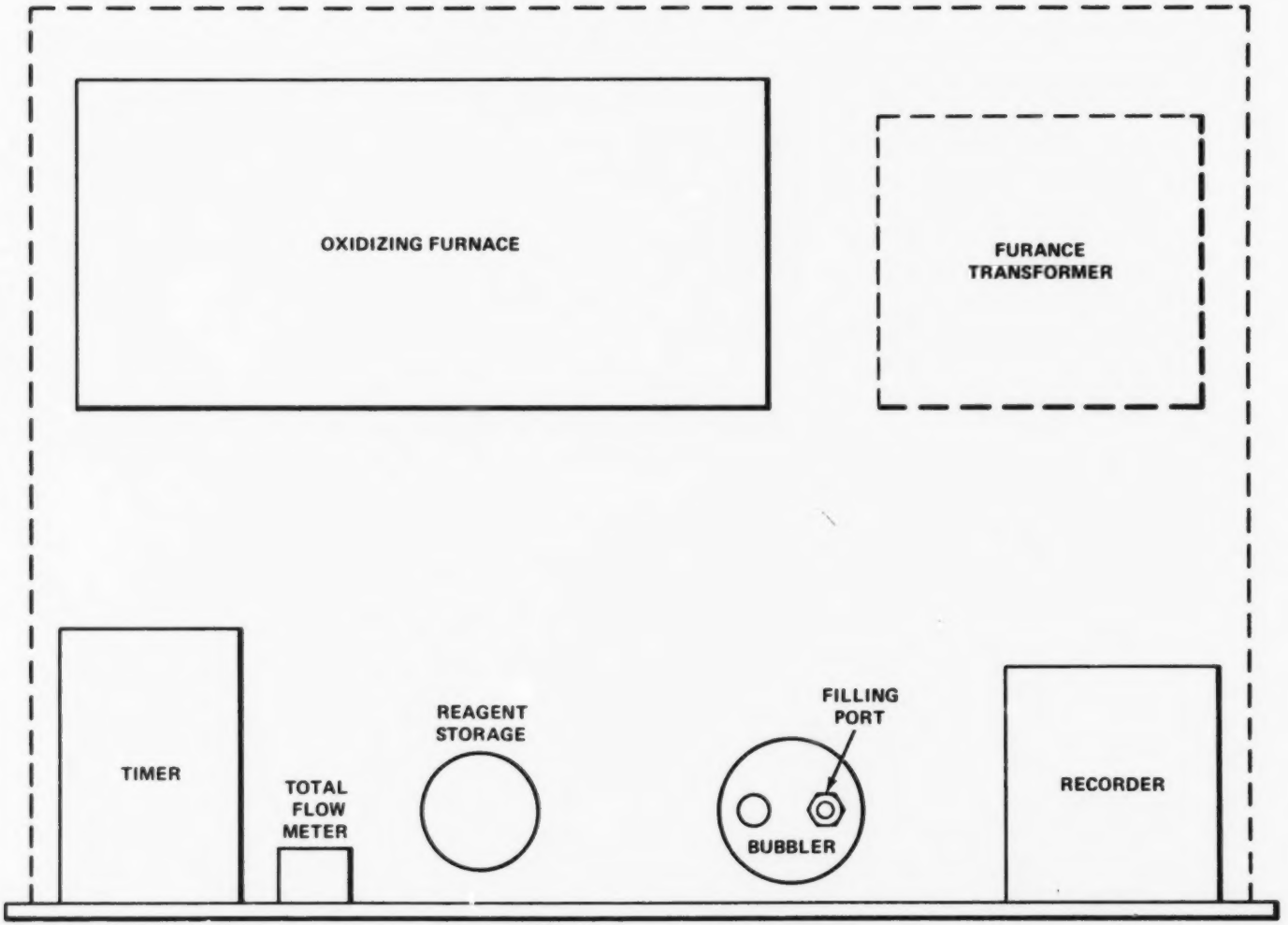

Figure 25 - Analysis System Components

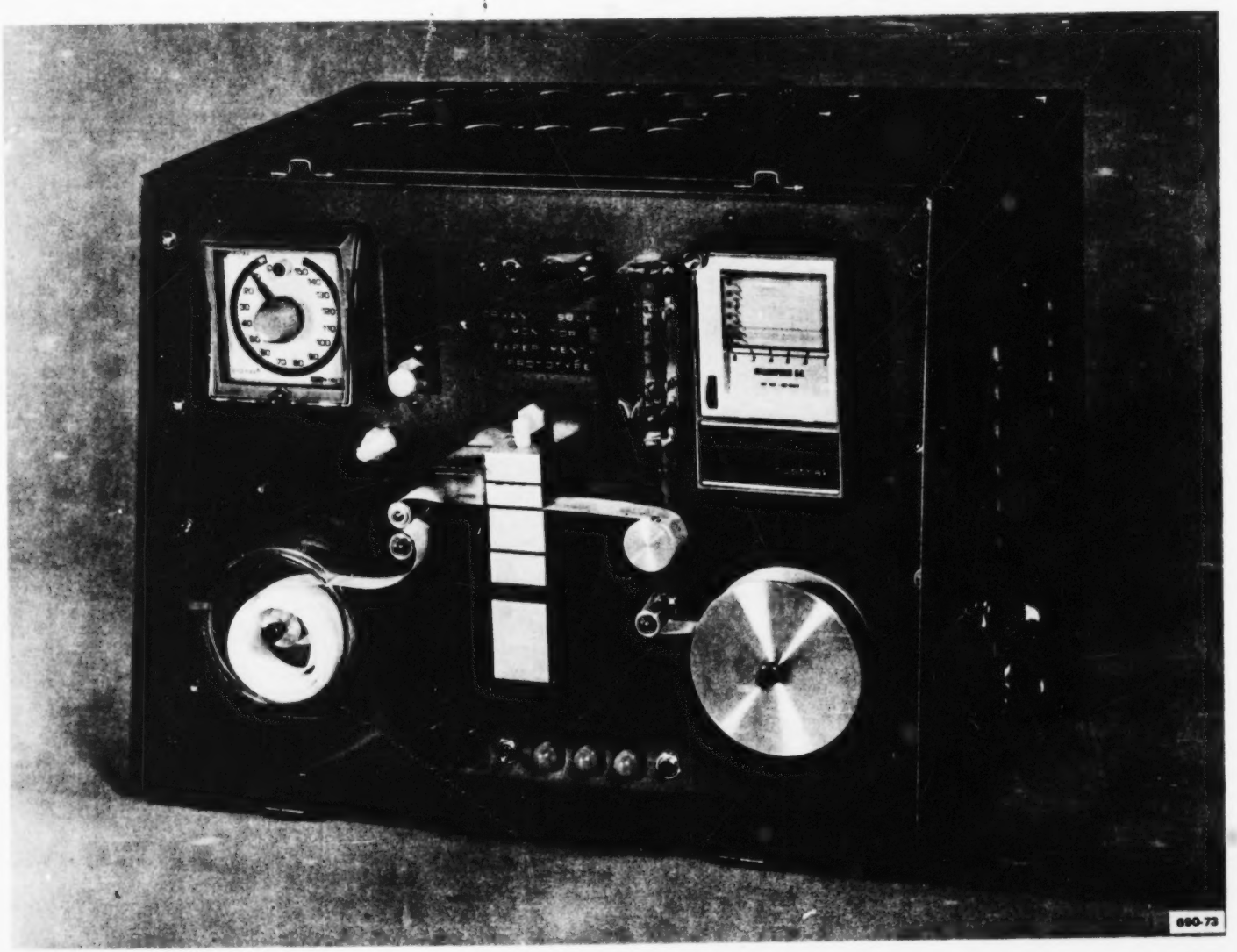

Figure 26 - Organic Sulfur Monitor

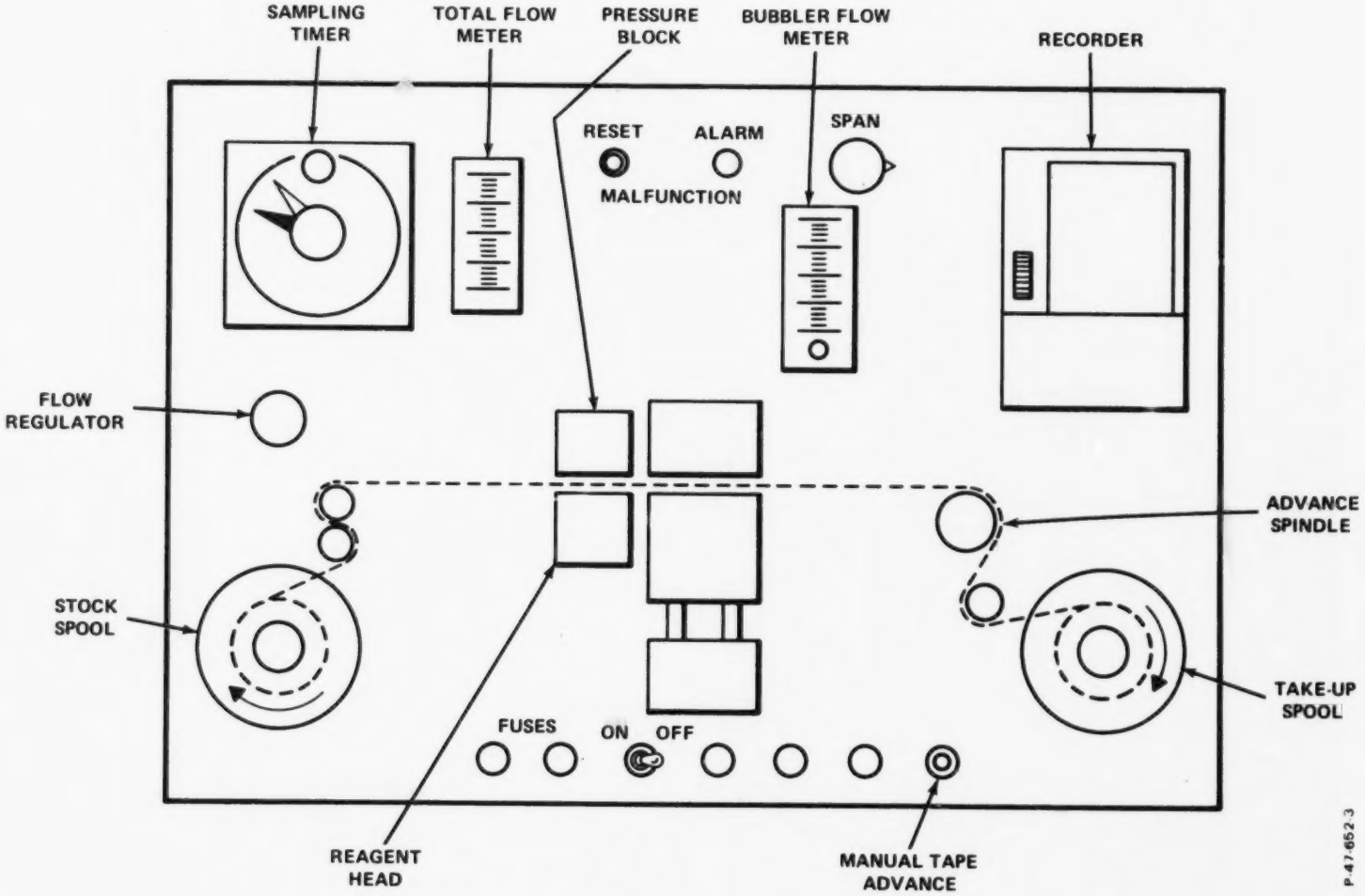

Figure 27 - Organic Sulfur Monitor

and record continuously the SO_2 in the oxidized sample air. Increasing or decreasing the total sampling time then permitted covering a concentration range from 10 ppm to over 10,000 ppm SO_2 if necessary.

7.3 LABORATORY TESTS

Initial experimental laboratory tests were made with standard SO_2-Air mixtures to establish the collection and measuring technique. Tests with ethanethiol solutions, in a heated bubbler to assure complete volatilization of the sample, verified the operation of the oxidizing furnace. The original plan to use pre-impregnated tape proved impractical because of the inherent reducing nature of the paper tape. Even acid-washed tapes retained enough reducing capacity to cause an intolerably rapid increase in background (blank) color development. Tape impregnated with the ferric ammonium sulfate and ortho-phenanthroline mixture remained stable if kept refrigerated below -10°C. At room temperature (24°C), however, the impregnated tape developed is full background color in 6 hours. Figure 28 compares blanks from tapes stored in a refrigerator and at room temperature.

Adding the reagent to the tape just before starting collection and measurement provided the best general solution to the background color problem. In addition to eliminating storage problems, the reagent addition technique permitted the use of standard, commercial paper tape as received. This technique also supplied some of the water to the tape, needed in the collection-measuring reaction, as part of the reagent solvent. With all the reagents present in the tape during sampling, the problems of irreproducible spot development and color elution were circumvented; as long as the tape was uniformly wetted by the reagent, the spots formed completely and reproducibly. Because of this, the sulfur monitor is potentially the most precise and accurate of the tape samplers.

Without the intermediate step of reagent addition, the recorded chart of sulfur monitoring was simplified as shown in Figure 29. Only the tape advance introduced stray points; the remaining points all represented opacity measurements on a continuing basis as SO_2 from the oxidized sample gas collected and reacted on the tape. The small tungsten lamp in the uppermost portion of the sampling-measuring head illuminated the tape during collection; the photoconductive cell beneath the tape recorded the opacity increase as the reaction took place on the tape. Any marked change in sulfur concentration in the sample gas during sampling changed the slope of the opacity curve. Collecting too long or using too high a sulfur concentration with a low span setting (low sensitivity) caused the opacity curve to stop rising as the tape reagent became exhausted. A 10 min collection time at 1.0 to 1.5 ℓ/min sample gas flow was selected for routing tests in comparing laboratory and plant tests.

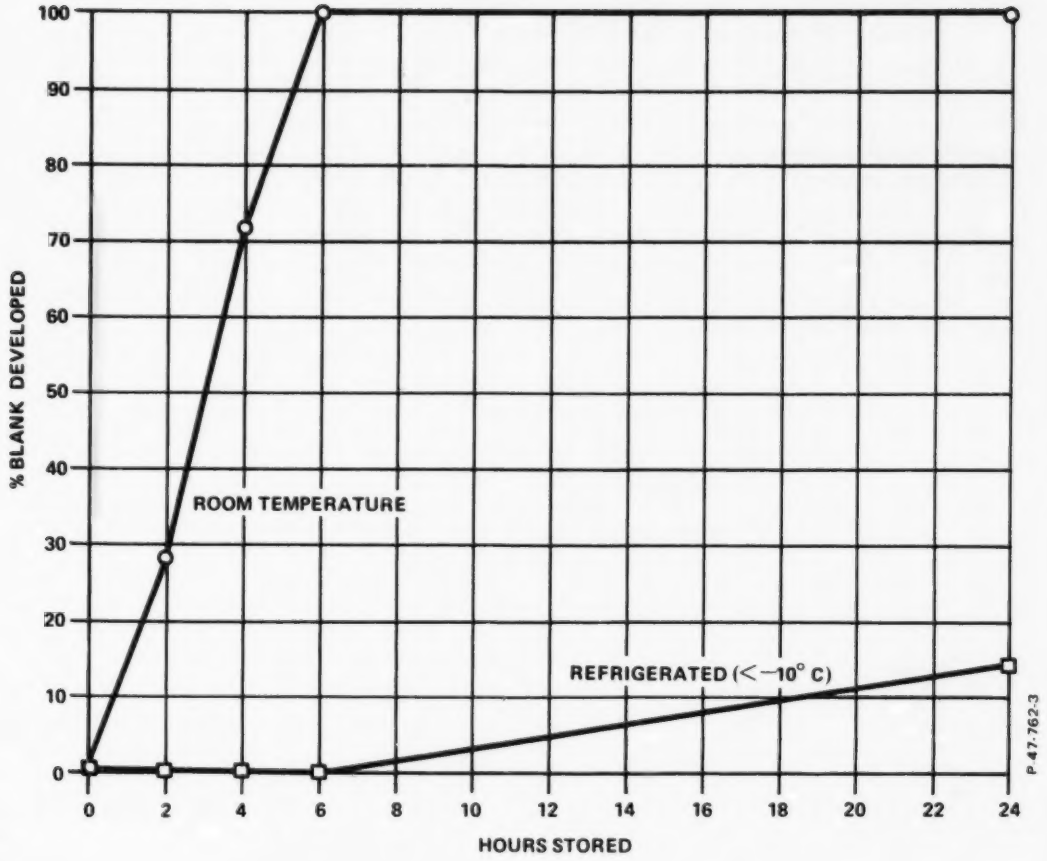

Figure 28 - Blank Development in Sulfur Tape

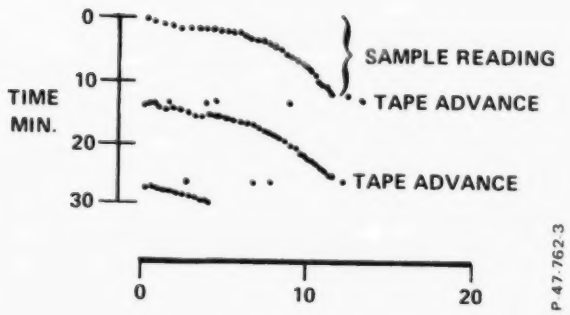

Figure 29 - Organic Sulfur Recordings

Figure 30 compares recorder readings for consecutive samplings of 90 ppm SO_2 drawn through the complete analytical train first with the oxidizing furance off (cold) and then at temperature (600-650°C). The first set of data, including all readings, averaged 15.8 with a standard deviation of 4.5. The second set, again including all the readings, averaged 19.8 with a standard deviation of 5.1. Within these deviation limits, the copper oxide in the oxidizing furnace had no significant effect on the sample readings. Discarding the extreme readings, it had no effect at all. A series of 30 consecutive samples taken unattended in the laboratory showed a standard deviation of 5.3 with only one extreme reading.

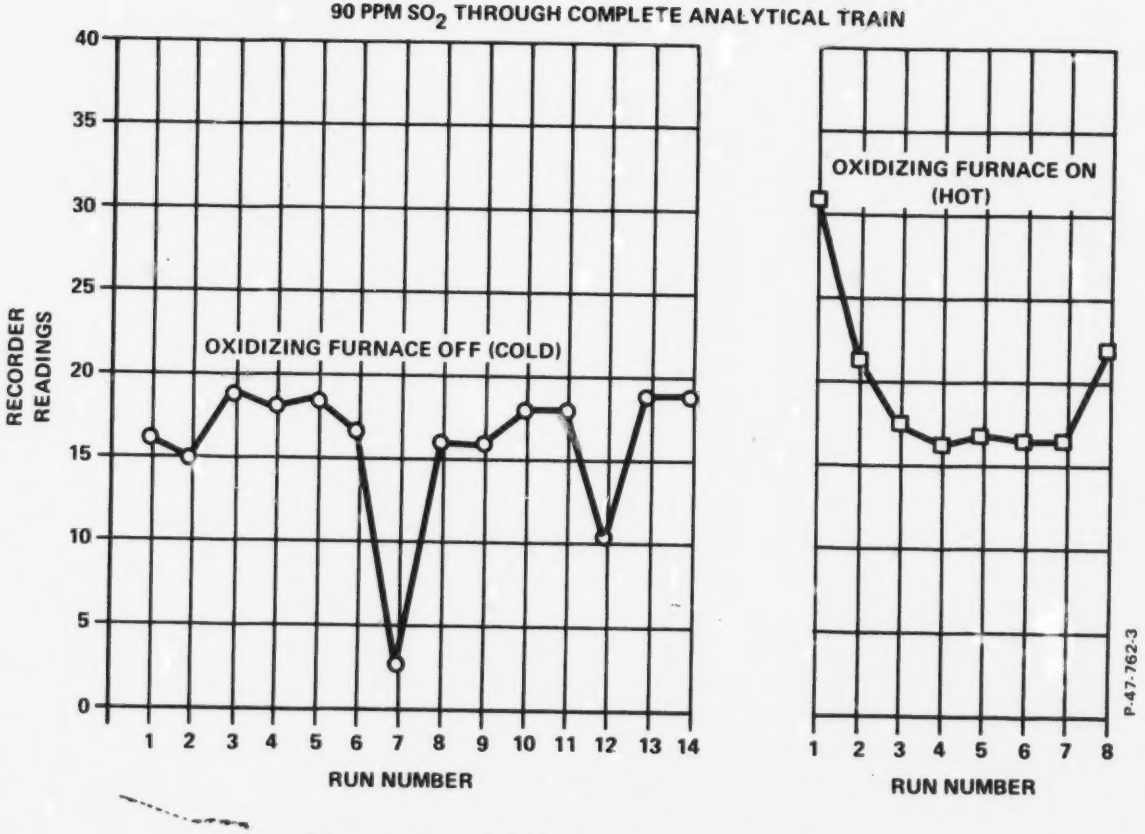

Figure 30 - Oxidizing Furnace Blank

SECTION 8

SUMMARY

All three tape samplers in their final design modifications performed well enough in laboratory tests to warrant field testing at a rendering plant. The aldehyde monitor showed the greatest deviation in readings, including the greatest number of extreme readings because of the inherent elution of the developing color compound by the flow of reagent in the tape. The reaction was sensitive enough, however, so that a change in the average over consecutive readings would show any large change in aldehyde concentration. Both the amine and sulfur monitors showed enough precision in their measurements to serve as continuous monitors of concentration drifts, as well as large changes, if the occasional extreme readings were ignored or if a running average was taken over consecutive samples.

The three monitors in their cases ready for field testing are shown in Figure 31. The flowmeters shown on the instruments were replaced with metric unit flowmeters to make recording of data in metric units easier. At the conclusion of the field tests, these instruments were delivered to the Project Officer.

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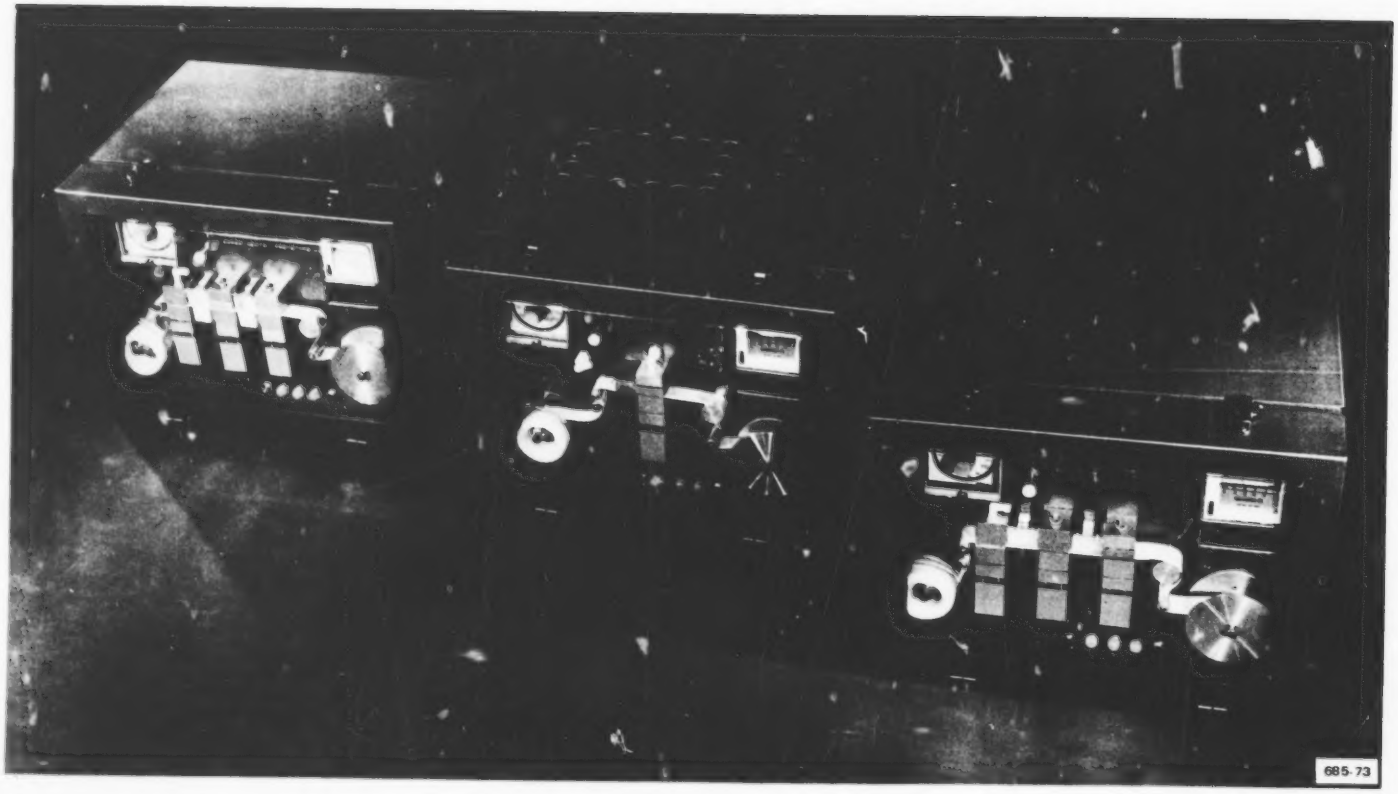

Figure 31 - Aldehyde, Amine, and Organic Sulfur Monitors
Ready for Field Testing

PHASE III

FIELD TESTING

SECTION 9

INTRODUCTION

Field tests were carried out at a local rendering plant to uncover any problems in the analysis method or instrument operation that environmental conditions in a plant might introduce. Sampling the vent for the press offered the most extreme environmental conditions in terms of ambient temperature, vibration, exposure to organic vapors, and assault from flying crackles, etc. A sampling line from the roof vent of a scrubber offered more general ambient operating conditions. Both these positions were used for continuous operating tests to check initial performance and the effect of subsequent modifications. The testing periods covered the first operating shift at the plant starting in late afternoon. This subjected the monitors to the greatest stress since plant temperatures and operating loads generally reached their peak between 5:00 p.m. and 8:00 p.m. during the test months (June and July). The sampling time was set at 10 min for all the plant tests.

Through the cooperation of Dr. Peter O. Warner at the local county air pollution control office, several concurrent odor samples, evaluated by an odor panel, were compared to monitor readings.

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SECTION 10

PROBLEMS AND MODIFICATIONS

An immediate problem appeared during the first attempts to sample exhaust gas from the cooker condenser. Condensed liquid, primarily water, occasionally carried into the condenser exhaust and then flooded the sampling system in the monitor. A simple cold-finger trap, operated at ambient temperature, placed in the sampling line acted as a convenient drop-out for the condensed water. This trap was used for collection at the press vent as well, but was not needed for sampling from the exhaust scrubber vent.

Ambient temperatures caused the other problems encountered in the plant tests. With both the aldehyde and amine samplers, evaporation of reagent from the reagent head increased as the ambient temperature increased, leading to missed spots or underdeveloped spots. This problem could be solved without any change in the instruments by increasing the delivery rate of the reagent syringe pump. The rate steps on the pump delivery control switch were small enough to conveniently compensate for the evaporation. Finer control was available through the adjustment on the interval timer cam but was not needed.

Overheating of the electronic components was the most serious problem uncovered by the field tests. When the monitors were operated beside the press vents in an area of poor air circulation, the ambient temperature reached 45°-50°C (115-122°F). Because the electronic components generate heat internally, they approached, and in the organic sulfur monitor sometimes exceeded, their 70°C (158°F) maximum rated operating temperature. This produced erratic response in the zeroing and measuring portions of the operating cycle. The rectifier bridges in the regulated power supplies were replaced with higher power units to avoid overloading at higher temperatures. The organic sulfur monitor, because of the presence of the oxidation furnace and its transformer, suffered most readily from overheating. Therefore, a small fan with a fiberglass filter was installed to circulate air across the electronic printed circuit boards.

No attempt was made to optimize the span, sampling rates, and analysis cycle for each instrument and sampling point to obtain optimum comparable data. Graphic comparison of some of the measurements, however, indicates the potential usefulness of the instruments for odor emission monitoring. The aldehyde measurements in Figure 32, despite their relatively large deviations, show a definite concentration difference between the laboratory samples and the plant samples. Figure 33 shows a copy of some of the recorded traces for these measurements along with a description of the plotting sequence. The numerical values with

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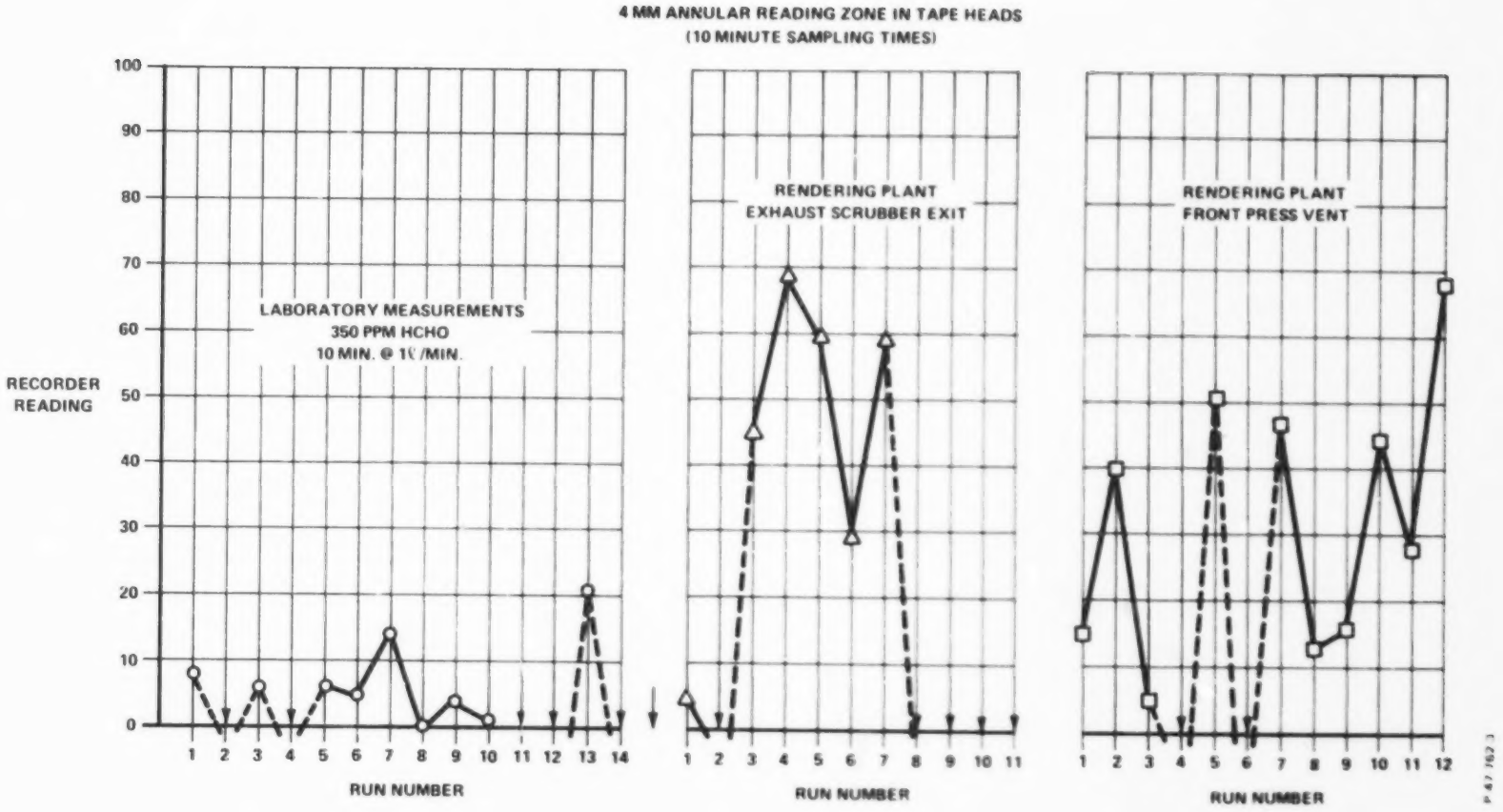

Figure 32 - Aldehyde Monitor - Plant Test Comparisons

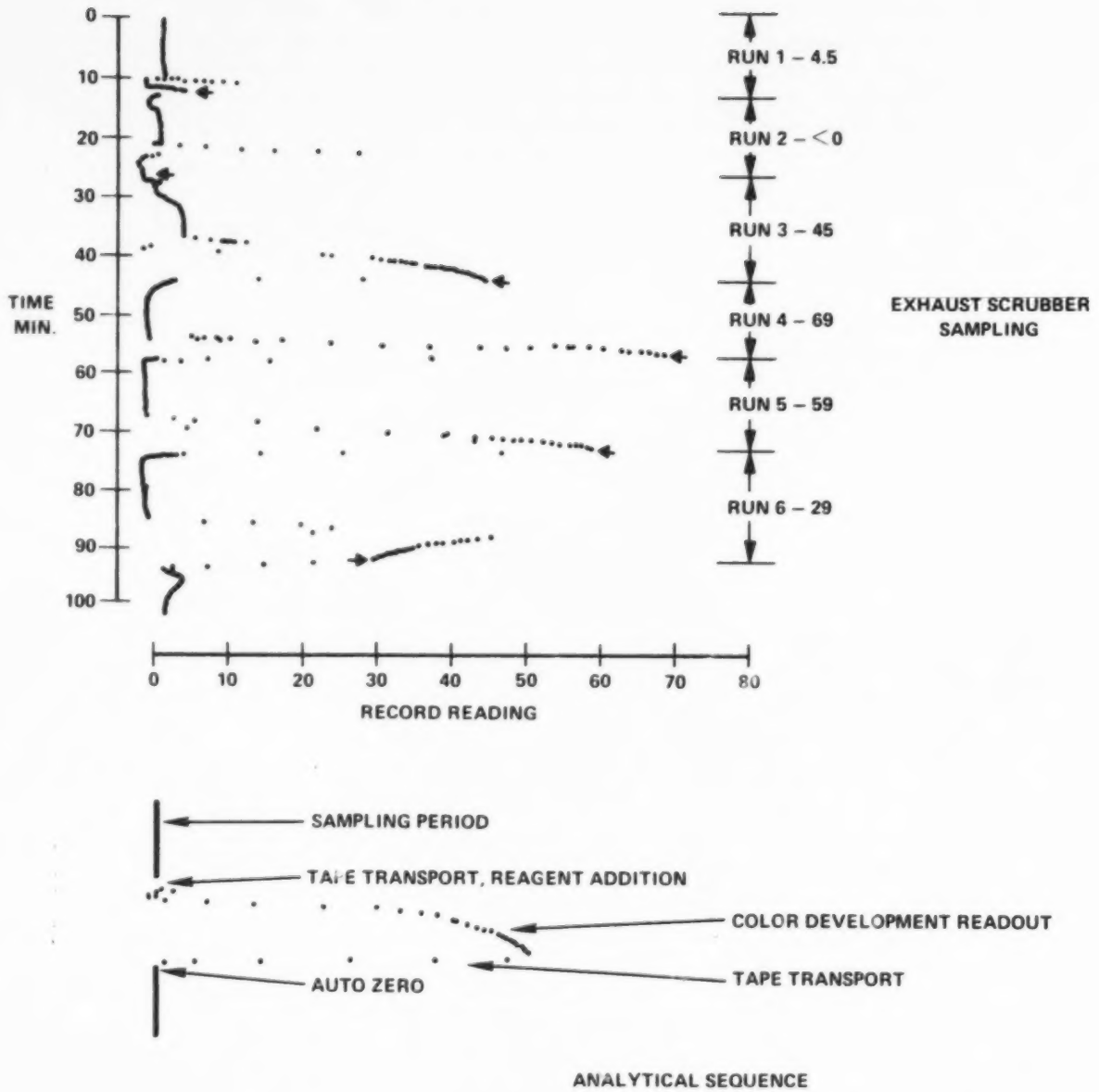

Figure 33 - Exhaust Scrubber Samplings

each run number designation give the recorder reading for that run, taken at the end of the color development readout. Visual observation of the spots on the tape confirmed the high aldehyde concentrations.

The measurements plotted in Figure 34 from some of the amine analysis tests clearly show the low concentration of amines in the exhaust scrubber exit gas, the consecutive readings averaging about the same as the laboratory blanks. The amine concentration in the press vent air varied both during a shift and from night to night as the measurements from two different nights show. The organic sulfur measurements showed less variation and were generally lower than the 90 ppm SO_2 readings obtained in laboratory measurements. Figure 35 shows some exhaust scrubber and press vent sulfur measurements compared to a series of laboratory measurements.

The ability of the tape monitors to produce consistent measurements under the most adverse plant conditions (the press vent measurements in these tests) indicates that they are potentially suitable for direct plant odor emission monitoring.

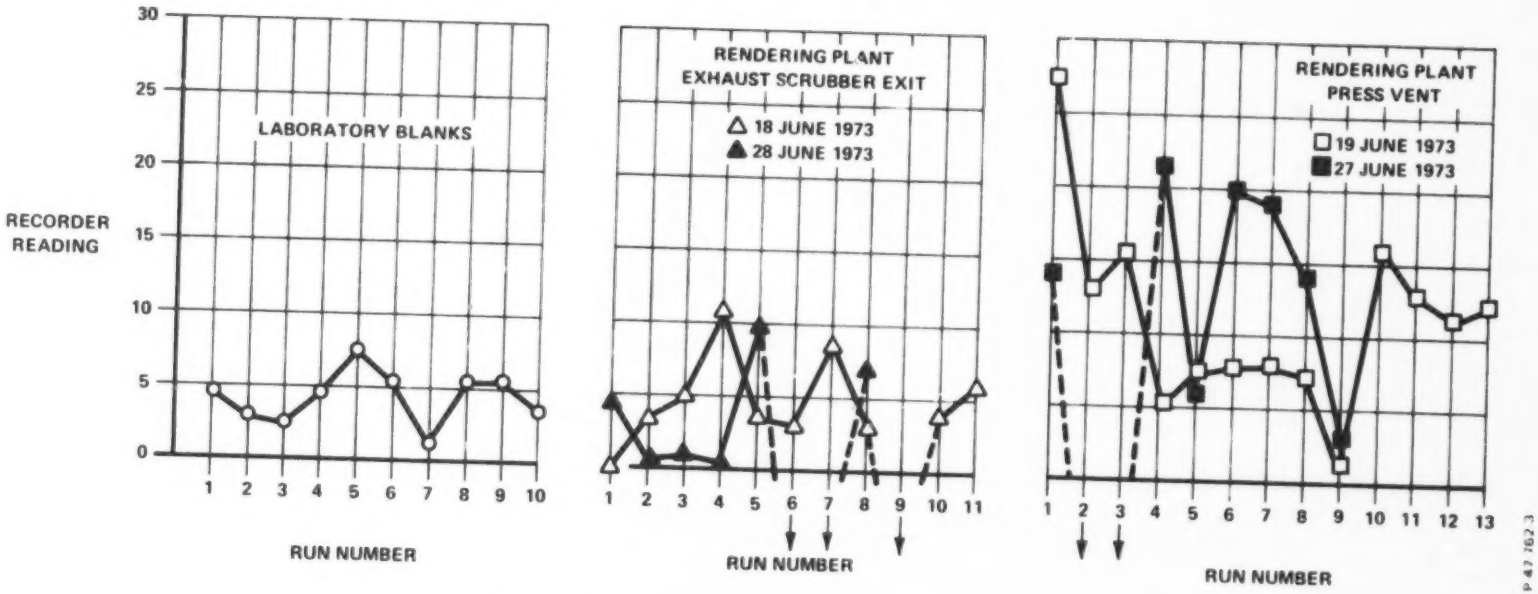

Figure 34 - Amine Monitor - Plant Test Comparisons

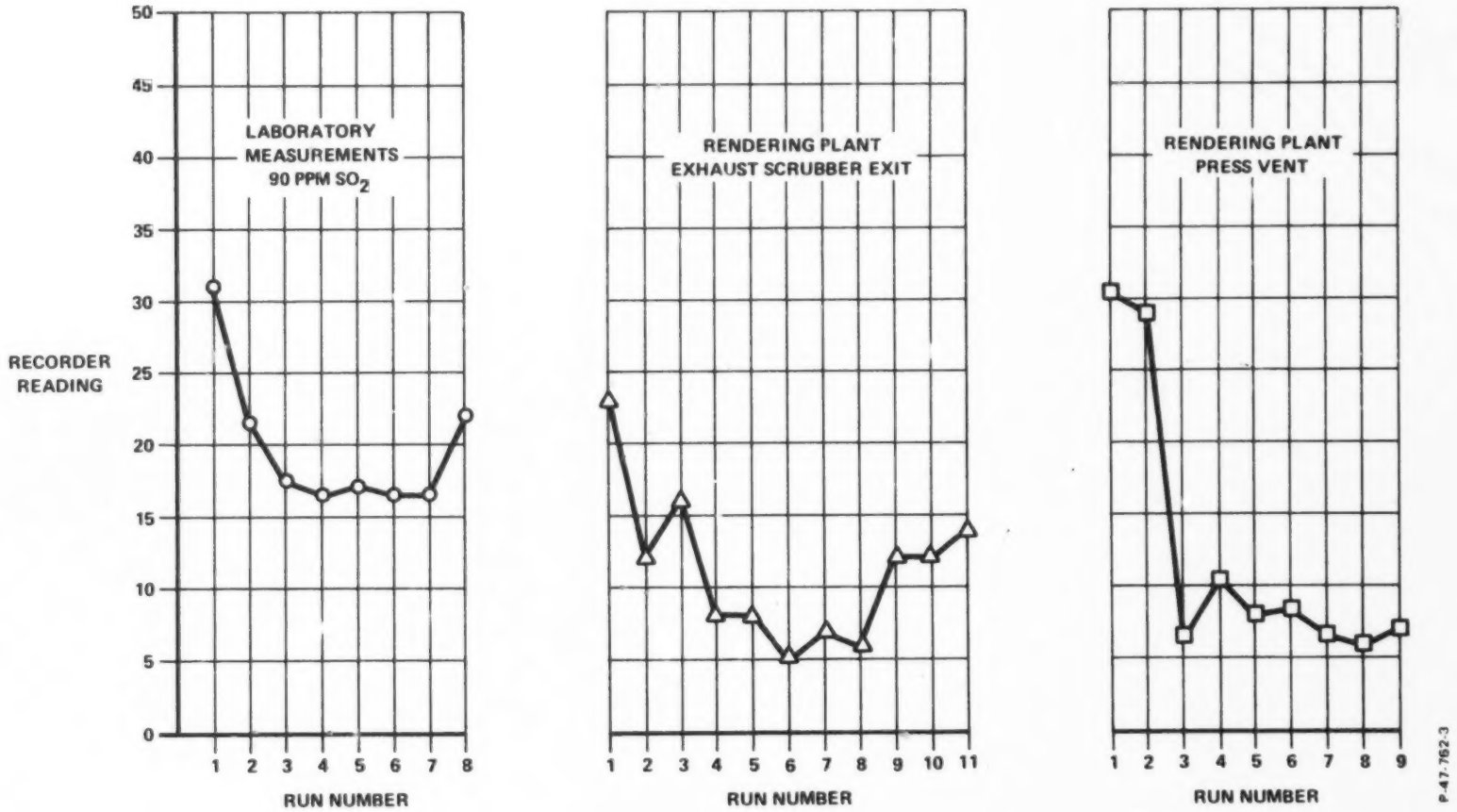

Figure 35 - Organic Sulfur Monitor - Plant Test Comparisons

SECTION 11

ODOR PANEL COMPARISON

As a trial comparison, four odor samples taken concurrently during the field testing were evaluated by an odor panel. With only one monitor at each of the two sampling points, intercomparison of the different classes of compounds or synergistic interactions could not be considered. This, of course, would require a full project in itself.

Dr. Peter O. Warner of the local county air pollution control office took the odor samples using 0.25 ℓ gas pipets. An odor panel, assembled according to guidelines of Benforado, Rotella, and Horton,[3] evaluated the samples using the ASTM dilution method D1391-57. Table 7 gives the results of the comparison. The only immediate conclusions to be drawn from the comparison is that the sulfur compounds did not appear to interfere with odor detection of other odorous compounds and that the monitors could record concentrations at or below the Federal guideline concentration of 5.6 OU/m^3 (200 OU/ft^2).

Table 7 - Comparison of Odor Levels and Monitor Readings

Sampling Point	Monitor	Reading	Odor Level, OU/m^3
Press Vent	Amine	20	3.14×10^7
Scrubber	Amine	0.5	4.25
Press Vent	Sulfur	8.5	4.42×10^7
Scrubber	Sulfur	8.0	3.03

SECTION 12

SUMMARY AND CONCLUSIONS

Collection and gas chromatographic analysis of emission samples from various process stages in a rendering plant revealed the presence of aldehydes, amines, thiols, organic sulfides, and organic acids as the major odorous compounds. Table 1 lists specific compounds found in the process emissions. The larger number of organic sulfur compounds and their particularly obnoxious odors gave them priority over the organic acids originally considered for monitor development in the program. Laboratory experiments showed that the MBTH aldehyde method, the ninhydrin measurement for amines, and the ferric ammonium sulfate-orthophenanthroline method for organic sulfur compounds (oxidized to SO_2) offered the best promise of adaptation for tape monitoring instruments.

Prototype monitors, based on modification of standard, commercial H_2S tape monitors, proved acceptable in laboratory tests for sensitivity and reproducibility. The aldehyde monitor showed the greatest deviations in readings because of inherent reagent-flow elution effects on color spot formation. 2-Methoxyethanol solvent for the amine-ninhydrin reagent gave acceptably uniform spot formation for amine monitoring. Adding both reagents for the sulfur determination to the tape just before sampling avoided any spot formation problem in the sulfur monitor.

Final testing of the monitors in a rendering plant led to minor modifications, primarily to prevent the electronic components from overheating under extreme conditions in the plant. All three monitors left unattended sampled and analyzed automatically in the plant tests. Comparison of several amine and sulfur monitor readings with odor panel evaluation of concurrent samples showed these instruments could record concentrations at or below the Federal guideline concentration of 5.6 OU/m^3 (200 OU/ft^3). The results showed that, despite the simplicity of the technique and inherent limitations of color spot methods, the instruments could serve as emission warning monitors for undesirable increases in odorous compound concentrations. The precision of the amine and organic sulfur monitors indicated that they could be considered for process control monitoring as well as for odorous emission concentration warning.

More extensive and systematic field tests are clearly indicated as the next step in developing this type of instrument for automatic, low-cost odor monitoring. Correlations between odor panel evaluations and the monitor analysis measurements or some combination of the amine, aldehyde, and organic sulfur measurements must be determined to establish the practical application of the instruments for plant emission monitoring. Once their practicality is established, redesign of the instruments,

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electronically and mechanically, should be undertaken to increase their endurance and performance ability under the extreme ambient conditions often encountered in plant operation. The redesign should also aim at reducing manufacturing costs so the final design will offer low cost instruments that can serve equally as on-line process control indicators and plant emission control, alarm, and compliance monitors.

SECTION 13

REFERENCES

1. "Part 23: Water; Atmospheric Analysis," Annual Book of ASTM Standards, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103, 1970.

2. Official Methods of Analysis of the AOAC, 11th ed., Association of Official Analytical Chemists, P. O. Box 540, Benjamin Franklin Station, Washington, D.C. 20044, 1970.

3. D. M. Benforado, W. J. Rotella, and D. L. Horton, "Development of an Odor Panel for Evaluation of Odor Control Equipment," J. Air Poll. Control Assoc., 19, 101 (1969).

4. T. A. Burgwald, Identification of Chemical Constituents in Rendering Industry Odor Emissions, Final Report, Project No. C8172, IIT Research Institute, 10 West 35 Street, Chicago, Illinois 60616, January 26, 1971.

5. Methods of Air Sampling and Analysis, Intersociety Committee, American Public Health Assoc., 1015 - 18th Street, N.W., Washington, D.C., 1972.

6. W. Leithe (translated by R. Kondor), The Analysis of Air Pollutants, Ann Arbor-Humphrey Science Publisher, Ann Arbor, Michigan, 1970.

7. W. E. Ruch, Chemical Detection of Gaseous Pollutants and Quantitative Analysis of Gaseous Pollutants, Ann Arbor-Humphrey Science Publishers, Ann Arbor, Michigan, 1970.

8. E. L. Piret and M. W. Hall, "Distillation Principles of Formaldehyde" Solutions, Ind. Engr. Chem., 40, 661 (1948).

9. E. Sawicki, "Photometric Organic Analysis" in Vol. 31 of Chemical Analysis, Wiley-Interscience, New York, 1970.

10. S. Siggia, Instrumental Methods of Organic Functional Group Analysis, Wiley-Interscience, New York, 1972, and Quantitative Organic Analysis via Functional Group, 3rd ed., Wiley-Interscience, New York, 1963.

11. F. D. Snell and C. A. Snell, Colorimetric Methods of Analysis, Vol. III, Organic-I, D. Van Nostrand Co., Inc., Princeton, New Jersey, 1962, and F. D. Snell, C. T. Snell, and C. A. Snell, Colorimetric Methods of Analysis, Vol. III-A, D. Van Nostrand Co., Inc., Princeton, New Jersey, 1967.

12. A. C. Stern, Air Pollution, Vols. I-III, 2nd ed., Academic Press, New York, 1968.

13. F. J. Welcher, ed., Standard Methods of Chemical Analysis, 6th ed., Vols. 2 and 3, D. Van Nostrand Co., Inc., Princeton, New Jersey, 1966.

14. E. L. Wick, "Volatile Components of Irradiated Beef," Chapter 2, pp. 5-18 in Exploration in Future Food-Processing Techniques, S. A. Goldblith, ed., MIT Press, 1963.

15. Zarazir, Chovin, and Guiochen, Chromatographia, 3, 180 (1970).